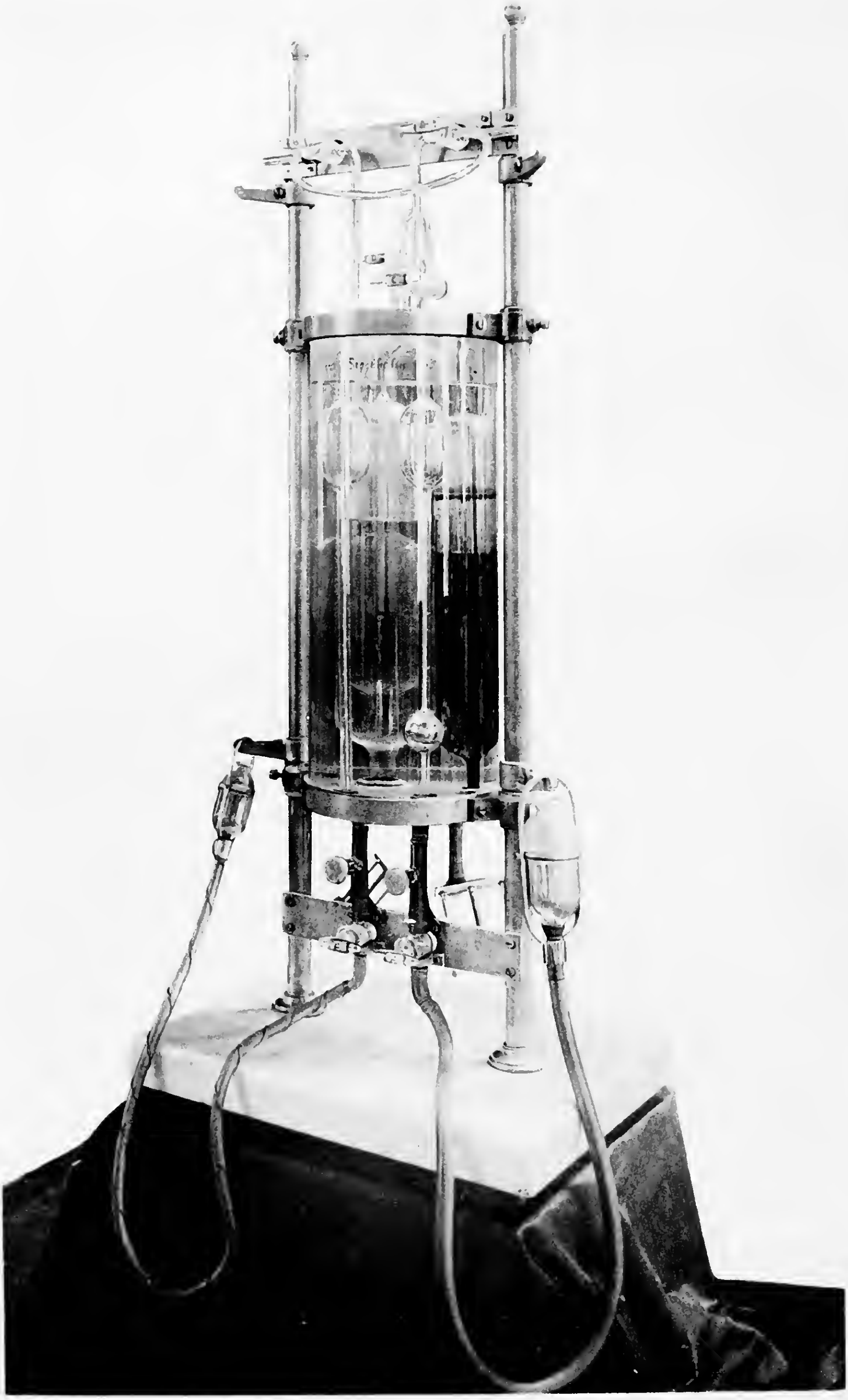

Apparatus for Analysis of Atmospheric Air, devised by Dr. Klas Sondén.

The Composition of the Atmosphere

With Special Reference to Its Oxygen Content

BY

FRANCIS G. BENEDICT

Director of the Nutrition Laboratory of the Carnegie Institution of Washington

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THE COMPOSITION OF THE ATMOSPHERE WITH SPECIAL REFERENCE TO ITS OXYGEN CONTENT

PART I.

AN HISTORICAL ACCOUNT OF THE DEVELOPMENT OF METHODS FOR DETERMINING OXYGEN.

The interest in meteorology and aeronautics—an interest ever increasing and international in scope—and the recent discoveries in the atmosphere of argon, helium, and their associated rarer gases, accentuate the fact that the present information regarding the oxygen content of atmospheric air, and, indeed, of the carbon-dioxide content, is far from satisfactory. The known sources of oxygen are very limited in number, for although it has been demonstrated that during certain periods of vegetative growth oxygen is liberated, the amount thus supplied to the atmosphere must of necessity be slight. On the other hand, the drafts upon atmospheric oxygen are constantly increasing. Taking into consideration those agencies that are directly or indirectly influenced by man, we see that since both the population of the world and the combustion of fuel are increasing enormously, this drain upon atmospheric oxygen must to-day be very much greater than, for instance, during the Stone Age. If, in addition, we consider the abstraction of oxygen by living organisms other than man, the oxidation of organic matter and decay, and the oxidation of iron, we find that all doubtless play an important rôle in decreasing the percentage of oxygen in the air. With these various agencies at work diminishing oxygen and producing carbon dioxide, it is to be expected that variations in the density of population, in the number of factories, in the distribution of vegetative tracts, and in the proportion of land and sea, would lead to like variations in the composition of the air. The nearest analogy to the atmosphere is sea-water, which, while vast in bulk, is known to have differences in composition at different depths and with different geographical distribution.

If changes take place in the composition of the air, of what nature are they? Are they measurable by our present methods of chemical analysis? Do these variations bear any relation to the changing seasons, to growth of vegetation, to rain, snow, and similar meteorological conditions, and to geographical location? These are questions that have long been in the minds of scientists, and, indeed, are to-day still debatable.

Alterations in climatic conditions have been ascribed by Arrhenius[1] to relatively small changes in the carbon-dioxide content of the air. Thus it seems that on meteorological grounds alone a study of the composition

[1] Arrhenius, Philosophical Magazine, 1896, pp. 237–276; also, Svenska Vetenskaps-Akademiens Förhandlingar, 1901, 58, pp. 25–58.

of air is well worth undertaking. But such a study, especially the study of the oxygen content of the air, has a still higher value in its relation to human life. No one chemical element enters so extensively into vital processes as does oxygen. The human body may live without food for many weeks; it may live without water for several days; but without air or oxygen it can live for only a very few minutes. Not only is oxygen essential to life, but the purity of the air is of fundamental hygienic importance. That this fact has been recognized is evidenced by the emphasis recently laid upon the necessity of an outdoor existence in combating tuberculosis. Furthermore, a knowledge of the composition of the air is necessary for the solution of the important problems of the ventilation of houses, mines, rapid-transit subways, and railroad tunnels. Of still more special significance, and with a more intimate bearing upon problems in physiology, is the fact that the determination of the oxygen consumption of man and important quantitative determinations in respiration experiments depend usually upon an exact knowledge of the composition of the air taken into the lungs. It is peculiarly fitting, therefore, that a study of this subject should be made a part of the scheme of research carried out in the Nutrition Laboratory.

The two forms of gas-analysis apparatus conceded by all experimenters to give the most exact results are the apparatus of Haldane in England and that of Sondén and Pettersson in Stockholm. Several forms of the Haldane apparatus are in the possession of the Nutrition Laboratory, and also a Sondén apparatus specially designed for the determination of carbon dioxide and oxygen in the air of the respiration chamber. This latter apparatus was devised by Dr. Sondén after a conference with the author in Stockholm four years ago, in which the various difficulties in the way of exact gas-analysis were carefully considered. With this apparatus the Nutrition Laboratory found itself in a position to carry out a more complete study of the percentage of oxygen in outdoor air than had hitherto been made. The ingenuity of Dr. Sondén and the technical skill of Miss Alice Johnson, of the laboratory staff, made such a study of atmospheric oxygen possible.

EARLY INVESTIGATIONS ON THE COMPOSITION OF AIR.

Although much has been written in recent years regarding the chemical composition of the atmosphere, there exists nowhere, at least in English, an historical account of the development of knowledge regarding the percentage of oxygen in the air; it is therefore deemed fitting to collect in this memoir the widely scattered records of the development of this most interesting subject.

The tenacity with which the belief in the elemental nature of air was held is well exemplified by the fact that not until the latter part of the eighteenth century did scientists begin to appreciate the fact that air consisted of two or more gases. This recognition of the composition of air

was unquestionably much retarded by the general acceptance of the phlogiston theory advocated by Stahl. According to the supporters of the phlogiston theory, all air had the same composition, but was more or less supplied with the "combustible essence" phlogiston. As a matter of fact, we find that the earliest investigators whose experimental evidence subsequently showed air to be composed of two or more gases, namely, Scheele, Priestley, Cavendish, and Lavoisier, all firmly believed in the phlogiston theory. Even after numerous roughly quantitative experiments had been made in which it had been demonstrated that the volume of air decreased after oxidation of material in it, scientists were loath to give up the phlogiston theory, and air was said to be more or less phlogisticated. Although a diminution in volume was observed when air was exposed to certain substances, such as alkaline sulphides, moist iron filings, phosphorus, or nitric oxide, this loss was simply considered as due to a portion of the atmosphere which was not saturated with phlogiston.

Scheele, noting the fact that the specific gravity of the air after absorption by various reagents had not altered, concluded that the decrease in bulk could not be due, as he first supposed, to the absorption of phlogiston, and that the atmosphere must of necessity consist of two distinct fluids. Although at first a strong supporter of the phlogiston theory, Lavoisier in 1777 enunciated the belief that the air consisted of two gases, one nitrogen (azote) and the other at first called dephlogisticated air, but finally known as oxygen; thus, for the first time, the definite existence of two distinct elemental components of the atmosphere was made clear. This observation soon led Lavoisier to the belief that all the phenomena of combustion could be explained on the basis of oxygenation without reference to the existence of phlogiston. Cavendish did not accept this new conception of the composition of the air until a number of years later, and even then his acceptance was far from a complete surrender. The one man, Priestley, who, perhaps more than anyone else, illuminated our knowledge of the atmosphere by his discovery of oxygen, advocated the phlogiston theory until his death in 1810.

It is thus clear that the dephlogisticated air of the earlier scientists was nothing more nor less than what we now call oxygen, and hence, although many of these writers considered the diminution in volume produced by the various reagents as an index of the amount of dephlogisticated air present, their observations have a certain historical value as indicating approximately the estimation of the amount of oxygen in the air by the methods then current.

The earliest observations of the quantitative relationship between the dephlogisticated air and the phlogisticated air were undoubtedly made simultaneously by Priestley in England and Scheele in Sweden.[1] Scheele's

[1] According to the published notebooks and laboratory records of Scheele (Carl Wilhelm Scheele, Efterlemnade bref och anteckningar, Utgifna af A. E. Nordenskiöld, Stockholm, 1892), his experiments must have antedated Priestley by two or three years.

experiments were wonderfully comprehensive and included a determination of the decrease in volume of a confined mass of air not only when mixed with nitric oxide but when subjected to the action of alkaline sulphides, moist iron filings with and without an admixture of sulphur, phosphorus ignited and at room temperature, and precipitated ferrous hydroxide. His experiments with alkaline sulphides were somewhat more extensive than with the other agents. In the first experiment he dissolved alkaline liver of sulphur in water, poured 4 ounces of the solution into a 24-ounce bottle, which he corked well, then reversed the bottle, and immersed its neck in a small vessel of water, keeping it in this position for a fortnight. At the end of this time, without removing the bottle from the water, he took out the cork, and the water at once rushed into the bottle. By noting the amount of water thus added he was able to demonstrate that in a fortnight, out of the 20 volumes of air in the bottle, 6 volumes were lost. In a second experiment he reports that 4 parts were lost out of 20, and at another time, when the bottle was corked for 4 months, there were 6 parts lost out of 20. As the result of the third experiment agreed with the first, the average of the three experiments shows a loss of approximately 6 parts out of 20, or 30 per cent. Scheele also exposed phosphorus to a confined volume of air, allowing it to remain for 6 weeks, and found that one-third of the air was lost.

Of particular significance in the light of the main purpose of this memoir is the fact the Scheele was the first to attempt a systematic study of the composition of the atmosphere over a lengthy period. In 1779 he communicated to the Academy[1] in Stockholm the results of his investigation of the preceding year. This communication was deemed of great importance by Lavoisier.[2]

The method employed by Scheele was to expose a confined volume of air to the action of a mixture of 2 parts of iron filings and 1 part of powdered sulphur, to which had been added a small amount of water. This mixture produced in a few hours a diminution of the air greater than that obtained by the sulphuret of potassium in several days.[3] Scheele used this method to determine the degree of salubrity of the atmosphere at different times of the year and to find out the proportion of "vital" air.

From January 1 to March 23, 1778, atmospheric air was found to contain 27.3 per cent of oxygen; on March 23, 24.2 per cent; on April 19, 20, and 21, 30.0 per cent. During the months of May and June the quantity of vital air was between 24 and 27 per cent; on October 5, during a very heavy storm, it was found to be 30 per cent. From October 5 to November 4 the quantity of vital air was 24 to 27 per cent; and on November 4 and 5, with the barometer very high, it was 24 per cent. From November

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[1] Scheele, Kongl. Vetenskaps-Academiens Handlingar, 1779, **40**, p. 50.

[2] Lavoisier, Recueil des Memoires de Lavoisier, **3**, p. 154; and Oeuvres de Lavoisier, 1862, **2**, p. 715.

[3] A figure of Scheele's apparatus is also given in F. Hoefer's Histoire de la chimie, 2d ed., Paris, 1869, **2**, p. 455.

5 to 20, the quantity of vital air was 24 to 27 per cent; on November 20 30 per cent, and on November 21, 24 per cent. During December the quantity of vital air was constantly between 24 and 27 per cent.

Scheele's investigation slowly but surely claimed the attention of scientists in other countries. In this connection it is of interest to quote the words of Dr. Joseph Black:[1]

> But Scheele was the first person who, from a number of ingeniously contrived experiments, concluded by very fair reasoning that atmospherical air is a mixed fluid composed of about two parts of azotic gas, and one part of vital air or oxygen gas, along with a very small admixture of carbonic acid.

The ingenuity and industry of this great Swede may properly be considered as having started the investigation of the composition of the air—an investigation that has had almost the continuous attention of chemists for over 130 years.

THE NITRIC-OXIDE EUDIOMETER.

Contemporaneously with Scheele, Priestley in England published several volumes of his "Observations on Air." In 1772 Priestley observed that when nitric oxide, prepared a number of years before by Stephen Hales, was added to common air confined in a vessel over water, a diminution in volume resulted. Experimenting in this way, Priestley showed that about one-fifth of the air combined with the nitric oxide and was absorbed by the water.[2]

Priestley's discovery of oxygen, which he found by heating the red oxide of mercury, was made on August 1, 1774. He was so wedded to the phlogiston theory, however, that he could only consider this oxygen as dephlogisticated air; hence its elemental nature was never admitted by him. This discovery was shortly followed by researches on the relationship between oxygen and the vital processes. It was early believed that the vital processes were more active in oxygen-rich air than in air that was deficient in oxygen; this stimulated innumerable investigations of the purity or salubrity of the air, chiefly by means of the simple nitric-oxide reaction of Priestley. The attempts to measure quantitatively the oxygen in the air early led to the development of special forms of apparatus for these measurements; as a matter of fact so extensively was the nitric-oxide test employed for studying the oxygen content of air, and so universal was the belief that the larger the amount of oxygen in the air the better was the air, that the instrument was actually designated an eudiometer, *i.e.*, a measurer of the goodness or salubrity of the air. As the dephlogisticated air supported respiration and combustion much better than ordinary air, it was natural to ascribe the healthfulness of the latter to the amount of dephlogisticated air present in it.

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[1] Black, Lectures on the elements of chemistry, 1st Am. ed. from the last London ed., 1806, **2**, p. 344. See also Scheele, Efterlemnade bref och anteckningar, edited by A. E. Nordenskiöld, Stockholm, 1892, p. 78.

[2] Priestley, Experiments and observations on different kinds of air, 1775, **1**, p. 111.

In considering the heterogeneous results reported by Priestley, it is important to note that the values he obtained were all comparative rather than absolute. He supposed that all samples of air had different quantities of dephlogisticated air in them; and if he took one sample of good air, compared it with a sample of questioned purity taken at the same time and at another place, and found that they underwent the same contraction in volume, he could assume that the two samples were equally pure. In other words, Priestley evidently failed to realize the significance of the contraction in volume. All of the observations of Priestley, then, were made distinctly upon the comparative rather than upon the absolute basis. He was, indeed, somewhat disturbed by the fact that air which theoretically was bad did not often show any deterioration.[1] He says on this point:

When I first discovered the property of nitrous air as a test of the wholesomeness of common air, I flattered myself that it might be of considerable practical use, and particularly that the air of distant places and countries might be brought and examined together with great ease and satisfaction; but I own that hitherto I have been rather disappointed in my expectations from it. My own observations have not, indeed, been many; but according to them the difference of the open air in different places, as indicated by a mixture of nitrous air, is generally inconsiderable; and I have reason to think that when very unwholesome air is conveyed to a great distance, and much time elapses before it is tried, it approaches, by some means or other, to the state of wholesome air. At least such I have found to be the case with the worst air that has at any time been sent to me in Wiltshire from distant manufacturing towns and workshops, etc., in them, where the air was thought to be peculiarly unwholesome. I am satisfied, however, from my own observations, that air may be very offensive to the nostrils, probably hurtful to the lungs, and perhaps also in consequence of the presence of phlogistic matter in it, without the phlogiston being so far incorporated with it, as to be discoverable by the mixture of nitrous air.

I gave several of my friends the trouble to send me air from distant places, especially from manufacturing towns, and the worst they could find to be actually breathed by the manufacturers, such as is known to be exceedingly offensive to those who visit them; but when I examined those specimens of air in Wiltshire, the difference between them and the very best air in this country, which is esteemed to be very good, as also the difference between them and specimens of the best air in the counties in which those manufacturing towns are situated, was very trifling.

Mr. S. Vaughan, senior, on his passage from Jamaica, brought me two bottles of air, one from the hold of the ship, intolerably offensive, the other the fresh air above deck in about 30′ N.; but the difference between these specimens of air, and the air of Wiltshire, was quite inconsiderable.

I have frequently taken the open air in the most exposed places in this country at different times of the year, and in different states of the weather, etc., but never found the difference so great as the inaccuracy arising from the method of making the trial might easily amount to, or exceed.

This recognition of at least the existence of a limit of accuracy for his method was unfortunately not seriously considered by many of his contemporaries.

[1] Priestley, loc. cit., 1779, 4, p. 269.

The application of the nitrous-oxide method for determining the degree of phlogistication of the air as first brought out by Priestley immediately led to an extensive interest in this problem on the part of a number of investigators. As Priestley's observations were but roughly quantitative, the Abbé Felice Fontana[1] in Italy constructed an instrument permitting a much greater accuracy in the measurement of the contraction in volume and determined the quantity of oxygen contained in air by absorption with nitric oxide, obtaining results showing from 18 to 25 per cent. Using this instrument, a number of investigators began studying the absorption due to nitric oxide, an absorption that was shortly to be explained by the oxygenation theory of Lavoisier. Slight minor modifications of the apparatus and method were made by many scientists who appeared almost inordinately[2] occupied in the testing of air in various places.

Prominent among the users of this instrument was Marsiglio Landriani,[3] who in 1775 published a record of his investigation and first introduced the term "eudiometer," descriptive of the instrument devised by Fontana.

In a letter to Priestley, dated at Milan, November 17, 1776,[4] Landriani writes:

> Before you receive this letter I shall have sent you my eudiometer, together with a short memoir, explaining the use of the machine, in order to ascertain with exactness the wholesomeness of the air in any particular place. It is the same instrument that I made use of in my tour through Italy, in the course of which I have had the satisfaction of convincing myself that the air of all those places which, from the long experience of the inhabitants, has been reputed unwholesome, is found to be so, to a very great degree of exactness, by this instrument of mine, so that the theory seems to correspond very well to observation. In the mountains near Pisa I made trial of the air at different heights, beginning on the plain, and proceeding to the highest summits; and found a remarkable difference in the state of the air, every stratum being purer in proportion as I ascended.

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[1] Felice Fontana, Descrizioni ed usi di alcuni stromenti per misurar la salubritá dell' aria, Firenze, 1774.

[2] For 20 to 30 years after Priestley's first discovery of the nitric-oxide eudiometer, it would appear from the innumerable references in the literature that every scientist of reputation, and many with no reputation, attempted air-analyses. Writing in 1912, one can but compare proportionally the number of those using the various forms of eudiometer 130 years ago with those to-day using wireless telegraphic apparatus. Priestley has summed up the situation admirably in the following sentences from the preface to volume 3 of his "Experiments and observations on different kinds of air," 1777:

"Those of my readers who may wish that I would still give a principal attention to this branch of experimental philosophy, will the less regret my discontinuing it, when they are informed with how much ardour and ability these pursuits are now prosecuted in very different parts of Europe.

"I am also informed by my friend Mr. Magellan, who frequently visits, and has a very extensive correspondence with the Continent, so as to be well acquainted with the present pursuits of philosophers, and who has himself taken pains to instruct many ingenious foreigners in the best methods of making experiments of this kind, that many other persons, whose names are at present unknown to the public, are at this very time assiduously employed on the same subject."

See also Johann Andreas Scherer, Geschichte der Luftgüteprüfungslehre, Vienna, 1785, 2, p. 74.

[3] Marsiglio Landriani, Richerche fisiche intorno alle salubritá dell' aria, Milano, 1775.

[4] Translated and printed in Priestley's Experiments and observations on different kinds of air, 1777, **3**, p. 380.

Among other early modifications of the nitric-oxide eudiometer are those of Magellan.[1] These are also referred to in a postscript in a letter to Priestley,[2] dated London, November 30, 1776, in which he writes:

> The other contrivances I want to show you are two new eudiometers to measure the degree of the salubrity of the air in different places. One of them, which I reckon the better, being the more simple and the neater of the two, is according to the original idea of your experiments on this subject; but in neither of them do I make use of any *cock*, both on account of its being difficult to be made, and likewise subject to be out of order. Those of Mess. the Chevalier Landriani and the Abbé Fontana seem to be liable to this inconvenience. The experiments already made in most parts of Italy by the former of those gentlemen, with his own eudiometer, deserve the greatest praises; and it is to be wished that philosophers would more generally apply themselves to this interesting subject of inquiry.

Dobson's[3] instrument was used for analyzing the air of "sea weed pods" and also, for comparison, the air of Liverpool.

Lavoisier[4] reports three experiments made with nitric oxide in which he found 25.3, 25, and 25.2 per cent of oxygen, respectively, an agreement which he says he had not dared to hope for. From these results, therefore, he concludes that the atmosphere, as he had previously announced, consisted of about 3 parts of mephitic air and 1 part of vital air. In 1777 Lavoisier made determinations of the quantity of vital air contained in the atmosphere and found it to be about 27.5 parts in 100, but maintains it is possible that this larger quantity of vital air depends upon the season.

Undoubtedly this quest for air with the highest oxygen content led to innumerable analyses of atmospheric air in the latter part of the eighteenth century which otherwise would not have been made. We find that Cavendish is reported as having made over 500 analyses of air by the nitric-oxide eudiometer before 1790.[5] Similarly the method was employed "daily for three years" by de Saussure[6] in a comparison of this method with the phosphorus eudiometer which was later to play an important rôle in air-analyses.

While many observers early found difficulties in the nitric-oxide method and soon discarded it for other methods, it seems to have been reserved for the genius of Cavendish so to adjust the conditions of experimentation with this agent as to secure approximately accurate information regarding the proportion of oxygen and nitrogen in the air. His results are marvelously accurate when judged by analyses made by the most approved methods of modern times. Cavendish was more interested

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[1] J. Hyacynth de Magellan, Description of a glass apparatus for making mineral waters like those of Pyrmont Spa, Seltzer, Seydschnitz, etc., together with the description of some new eudiometers, etc., London, 1777.

[2] Priestley, loc. cit., 1777, **3**, p. 379.

[3] See Dobson's letter to Priestley, loc. cit., 1779, **4**, p. 469.

[4] Lavoisier, Memoires de l'Academie des Sciences, 1782, p. 486. See also Oeuvres de Lavoisier, 1862, **2**, p. 503.

[5] Wilson, Life and works of Cavendish, London, 1851, p. 227.

[6] de Saussure, Journal de Physique, 1798, **47**, p. 470. See also Gilbert's Annalen der Physik, 1799, **1**, p. 505.

in knowing the *amount* of the decrease in volume than the *cause*. With his keen insight and experimental technique he attacked the problem, and in 1783 published a paper describing a new eudiometer. By carefully noting the rate and the amount of nitric oxide used with this apparatus and particularly by adding the air to a previously measured amount of nitric oxide, he was able to make a more careful examination and test of air. Of particular interest in connection with this paper are his words regarding the tests of air on different days:[1]

> During the last half of the year 1781 I tried the air of near 60 different days in order to find whether it was sensibly more phlogisticated at one time than another; but found no difference that I could be sure of, though the wind and weather on those days were very various, some of them being very fair and clear, others very wet, and others very foggy.

He also studied the air in different localities and compared the air of London with that of the country. Although Cavendish found some evidence to show that the air at Kensington was better than that in London, he nevertheless believed that the differences were no greater than the limits of experimental error, and taking the mean of all, that there was apparently no difference between them. The number of days compared was 20, the greater part of the samples being taken in cold winter weather, when there were a great many fires and but little wind to blow away the smoke. From figures given in Cavendish's notebook, Wilson[2] concluded that these observations established that the percentage of oxygen in the air was 20.83. This figure has been made much of in discussions of the percentage of oxygen in the air, but an examination of Cavendish's data shows that the limit of error was very large, and that he could not possibly have been inside of 1 or 2 per cent of the total amount of oxygen involved; hence a representation of his percentage of oxygen with four significant figures is without value. As Cavendish at that time paid no attention to the purity of the nitric oxide, although recognizing in a crude way the differences in quality and the possibility of combination with varying amounts of dephlogisticated air or oxygen, it is fair to conclude that the method could not possibly have had an accuracy closer than 2 per cent of the total. Cavendish was the first to establish that the composition of the air was essentially constant within the limits of his apparatus, and that it did not sensibly vary in different parts of the country. That it was possible to obtain these results with an instrument and a method with as great error as we now know them to have had is certainly most remarkable evidence of his skill as an experimenter.

Among others who extensively used the nitric-oxide eudiometer must be mentioned Ingen-housz, who, in his researches on plant life and on his travels, used a portable apparatus of his own devising.[3]

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[1] Cavendish, Philosophical Transactions, 1783, **73**, p. 126.
[2] Wilson, loc. cit., p. 41.
[3] Ingen-housz, Vermischte Schriften, 2d ed., Vienna, 1784, **2**, p. 242.

Van Breda[1] in Delft made analyses of air by the nitric-oxide eudiometer on 195 days in 1781 and 1782, but the results have little quantitative value.

In an address before the Academy in Barcelona on May 22, 1790, Antonio de Marti[2] announced the results of his experiments on the "Quantity of vital air in the atmosphere, and the different methods of measuring it." Among other means he used nitric oxide and reported uniformity in composition of the air.

> During some days of the year 1787, in which the common air experienced no variation by means of nitrous air, since 100 parts of each were uniformly reduced to 99 or 00, I was desirous of making a comparative trial of the same common air by means of iron and sulphur, and I observed that of 100 parts of air there remained from 79 to 81 and that consequently, from 19 to 21 hundredths had disappeared.

One of the most extensive contributors to our knowledge of the composition of the air obtained by means of the nitric-oxide eudiometer was Alexander von Humboldt, and in his records we find recognition of the existence not of dephlogisticated air but of oxygen, accepting Lavoisier's newest theory with regard to the air. von Humboldt recognized the importance of testing the purity of the nitric oxide used, and determined the degree to which it would dissolve in a ferrous-sulphate solution.

In 1798 von Humboldt[3] had analyzed the air collected in a balloon journey by Garnerin and Beauvais at an altitude of 1303 meters and compared it with the air of Paris, using nitric oxide and ferrous sulphate. The air in Paris showed 27.6 per cent oxygen and the balloon air 25.9 per cent. These balloon samples are of general interest in that they substantiate the simultaneous observations of de Saussure,[4] who, using a nitric-oxide eudiometer, analyzed air taken from the tops of several mountains. Though the results are not expressed numerically, de Saussure concludes that the air of mountains is somewhat less pure in vital air than that of the neighboring plains and valleys.

Although a large number of desultory investigations had been made by Ingen-housz in London, van Breda in Delft, Pickel in Wurzburg, Lampadius in Freiburg, Lichtenberg in Göttingen, Scherer in Vienna, and Breze, all of whom used the nitric-oxide eudiometer, yet von Humboldt[5] was dissatisfied with these researches, believing that analyses of the air should be accompanied by observations with regard to its elasticity, temperature, moisture, electricity, and clearness. He accordingly undertook an extensive series of observations with regard to the oxygen content of

[1] Letter to J. Ingen-housz, Vermischte Schriften, 2d ed., Vienna, 1784, **2**, p. 441.

[2] This lecture was translated into French and printed in the Journal de Physique, 1801, **52**, p. 173. Abstracted in Gilbert's Annalen der Physik, 1805, **19**, p. 389. The lecture was also printed in English in the Philosophical Magazine, 1801, **9**, p. 250.

[3] von Humboldt, Journal de Physique, 1798, **47**, p. 202.

[4] de Saussure, Voyages dans les Alpes, Neuchatel, 1803, **1**, p. 427.

[5] von Humboldt, Versuche über die chemische Zerlegung des Luftkreises, Braunschweig, 1799, p. 150.

air in Salzburg, using a nitric-oxide eudiometer. The close proximity to the Alps also enabled him to study the composition of air on the top of mountains as well as that in the valley.

Although we now know that von Humboldt's oxygen determinations were erroneous owing to the test used, namely, nitric oxide, nevertheless his observations and the tabular statement of his results have the completeness which characterizes modern scientific research, and in many ways the thoroughness of the investigation commends itself to modern workers. Using the Fontana eudiometer, he made observations of the air in Salzburg (1302 feet above sea-level), covering practically a whole year, the samples of air being taken for the most part from a garden on the south side of the city. Since this air might be considered contaminated, he compared it with that from the open country some distance from the city, but was never able to detect any difference. The results are expressed in tabular form at the end of his book, each value representing the average of 3 to 5 tests.

The analysis of the Salzburg air gave a range in oxygen content from 23.6 per cent to 29 per cent. The author concluded that the oxygen content can vary 5.4 per cent and does not always remain between 27 and 28 per cent. In observations on 144 days he found only 7 times that the oxygen rose above 28.1 per cent. The average oxygen content was:

	per cent		per cent
November	25.6	March	26.9
December	26.8	April	27.2
January	27.5		
February	27.2	Average	26.8

He came to the conclusion that in clear weather there is an increase in the oxygen, and as bad weather approaches there is a decrease.

He also made comparative observations of mountain and valley air. With the assistance of a friend, samples were taken simultaneously at noon from the Geisberg (3890 feet) and from the valley. On December 18, 1797, the mountain air gave 23.6 per cent of oxygen and the valley air 26.2, or 2.6 per cent of oxygen more than the mountain air. On January 30, 1798, another observation was made, the results for the mountain air being 26.1, and for the valley air, 27.4 per cent. On March 4, 1798, another set of samples gave for mountain air 26.4 and for valley air 27.3 per cent. On March 11, 1798, the results for the two samples were identical, namely, 26.4 per cent.

Assuming that the nitric oxide used by earlier experimenters was not below a certain degree of purity, von Humboldt computed the oxygen content of the air in several cities as follows:

	per cent
Vienna	26.1
Göttingen	26.6
London	26.9
Florence	25.3
Delft	27.0

He evidently wished to take into consideration not only the temperature of the air examined, but the possibility of differences in expansion, and referred to one of his researches indicating such a difference.

About the time that his book was published, von Humboldt started on a scientific expedition to Spanish America, and in a letter written by him to Delamétheric[1] from Cumana, South America, he shows his intense interest in the composition of the air, and in the possible sources of contamination or alteration of the oxygen content, by citing his experiment with a sample of air which he had collected in a bottle from the crater of a volcano. After having determined the purity of his nitric oxide by means of ferrous sulphate, he found only 19 per cent of oxygen in this sample, while at the sea-level the oxygen content was 27.8 per cent. The idea of a geographical difference in composition of the air was also evidently present, since he cites the fact that he was able to analyze the air on board ship with as much ease as in his laboratory, and found that the sea air at 10° 30′ "on a beautiful moonlight night" contained over 30 per cent of oxygen. So firm was von Humboldt's belief in the nitric-oxide eudiometer that he was in constant polemical discussion with Berthollet with regard to the relatively new phosphorus eudiometer.

As facility in experimental technique was acquired by scientists in the new field of pneumatic chemistry, errors in the nitric-oxide eudiometer were early recognized and it is not surprising to find Seguin[2] stating that this method has 20 different errors. Even von Humboldt,[3] its most ardent supporter, pointed out that nitric acid of different strengths yielded nitric oxide of different character which combined with different amounts of oxygen from the air. A few years later[4] he acknowledged completely the errors of the method, which he then discarded for the hydrogen eudiometer of Volta. Subsequently, Berger[5] in Geneva laid especial emphasis upon the errors of the nitric-oxide method and opposed von Humboldt's belief that the nitric-oxide solution in ferrous sulphate was a suitable reagent for accurate oxygen determinations, concluding that the phosphorus eudiometer was very much superior.

Although the original nitric-oxide method of determining oxygen was destined to be relegated to the ranks of impracticable chemical operations, the experience with it naturally led to the employment by Davy[6] of a solution of nitric oxide in ferrous sulphate. This means of testing the purity of the nitric oxide had been advocated by von Humboldt, and Davy first made use of the oxygen-absorbing power of such a solution to analyze air. Davy strongly criticized the old Fontana nitric-oxide eudiometer, but pointed out that 1 c.c. of a reasonably strong solution of ferrous

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[1] von Humboldt, Gilbert's Annalen der Physik, 1800, **4**, p. 443.
[2] Seguin, Annales de Chimie, 1791, **9**, p. 293.
[3] von Humboldt, Annales de Chimie, 1799, **28**, p. 123.
[4] von Humboldt and Gay-Lussac, Journal de Physique, 1805, **60**, p. 129.
[5] Berger, Journal de Physique, 1802, **56**, p. 253.
[6] Davy, Journal of the Royal Institution, 1802, **1**, p. 45.

sulphate saturated with nitric oxide would absorb 5 to 6 c.c. of oxygen. Comparative tests were made with phosphorus and alkaline sulphides.

In his analyses of atmospheric air with a saturated solution of nitric oxide, he never found a change in the constituents. The air on October 3, 1800, on the sea, at the mouth of the Severn, with a strong west wind blowing over the Atlantic Ocean, contained 21 per cent of oxygen. Exactly the same amount was found in air brought from the coast of Guinea to Dr. Beddoes by two Liverpool surgeons. Davy's ingenious use of the ferrous-sulphate solution of nitric oxide was short-lived, for he himself found that the alkaline sulphides always gave a somewhat larger absorption.

Allen and Pepys[1] employed the ferrous sulphate-nitric oxide method to analyze not only air, but some gaseous mixtures rich in oxygen. They report that outdoor air was continuously found to contain 21 per cent of oxygen.

The last writer to make any considerable use of the nitric-oxide eudiometer was Dalton,[2] who, comparing the Volta hydrogen eudiometer with the nitric-oxide eudiometer and the sulphide of lime absorption method, says:

> The nitrous gas eudiometer is of singular utility on many occasions. No other can exceed it in accuracy when mixtures contain very little, as one or two per cent of oxygen; or on the other hand when nearly the whole of the gas is oxygen. But when the mixture of gases contains from twenty to eighty per cent of oxygen, as in the case of common air, it is not the best when great exactness is required.

THE BEGINNINGS OF ACCURATE AIR-ANALYSIS.

The early historical interest attaching to the development and extensive use of the nitric-oxide eudiometer justifies the special treatment which has been given of this method; nevertheless other absorbents for oxygen were used. The large number of scientists experimenting daily with the newly discovered gas, oxygen, and acquiring information with regard to its properties, rapidly brought together a series of methods for determining this gas in air. While the nitric-oxide method has long been discarded as utterly worthless, the alkaline sulphides first employed by Scheele were for some time used in air-analyses, and phosphorus for absorbing oxygen, likewise employed by Scheele, has even to-day an extensive use. The explosion of air with hydrogen, first employed by Volta, has also withstood the critical attacks of over 100 years and to-day is much used.

As Scheele found from his experiments with different absorptive agents variations in the oxygen content of air, so Lavoisier likewise, using various agents, was unable to find any satisfactory value for the percentage of oxygen, for we find in his reports varying values assigned to the oxygen

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[1] Pepys, Philosophical Transactions, 1807, Part I, p. 247; Allen and Pepys, Philosophical Transactions, 1808, 8, p. 255.

[2] Dalton, Philosophical Magazine, 1838, 3d ser., 12, p. 158.

content of air. Lavoisier was infinitely more interested in chemical problems involving combustion in the air than he was in the exact composition of air itself, and hence we find his records of air composition always incidental to other important data.

Thus, in studying the properties of phosphorus,[1] he reports that in a large number of experiments in which an excess of phosphorus was burned in a bell jar containing 109 pouces[2] he found a diminution in volume of 20 to 21 pouces, that is, about one-fifth. Lavoisier also noted an increase in the weight of the phosphorus. Of particular interest is the experiment reported in his memoir on the respiration of animals,[3] in which he heated mercury with a confined volume of oxygen. On heating 50 pouces of common air with 4 ounces of mercury, he found at the end of 12 days that the air was diminished one-sixth part. In the same year, 1777, in his report of the research on the combustion of a candle,[4] he states that the air contains about one-fourth of its volume of "air pur et respirable." Finally, in 1785, in a report of a study of the alteration of air by respiration,[5] he maintained that air contains 25 per cent of oxygen.

Lavoisier's experience with all known methods for absorbing oxygen justified his critical discussion of the subject[6] in which he maintains that the eudiometers established on the principle which depends upon the great affinity between oxygen and phosphorus, or the alkaline sulphides, or the mixture of iron and sulphur, are much preferable to those of Priestley, Fontana, and Ingen-housz using nitric oxide. In the first place, it is always easy to have phosphorus, sulphur, and iron perfectly identical, while nitric oxide always differs in composition. Second, the nitric oxide does not always absorb all of the vital air. Third, this gas is susceptible of different degrees of oxygenation varying with the temperature and pressure, the rapidity of mixture, and the diameter of the vessel. Fourth, the nitric oxide is capable of mixing with nitrogen in all proportions. An excess of sulphuret of potash, iron, sulphur, or phosphorus may be used without affecting the results, but with nitric oxide an excess produces an error. Lavoisier finally decided to use sulphuret of potash, preparing the air sample over water and at the end of 15 to 20 days determining the contraction in volume. The importance of a general study of the oxygen content of the air on the earth is emphasized in the following paragraph from Lavoisier:

Il est à désirer que quelque physicien ait le courage d'entreprendre, par cette méthode, une suite d'expériences sur l'air atmosphérique recueilli dans différents lieux, dans dif-

[1] Lavoisier, Opuscules Physiques et Chimiques, 1773; Oeuvres de Lavoisier, **1**, p. 643.
[2] A cubic pouce equals 19.6 c.c.
[3] Lavoisier, Memoires de l'Academie des Sciences, 1777, p. 185; Oeuvres de Lavoisier, **2**, p. 174.
[4] Lavoisier, Memoires de l'Academie des Sciences, 1777, p. 195; Oeuvres de Lavoisier **2**, p. 184.
[5] Lavoisier, Recueil d. Memoires de Lavoisier, **3**, p. 13; Oeuvres de Lavoisier, **2**, p. 676.
[6] Lavoisier, Recueil d. Memoires de Lavoisier, **3**, p. 154; Oeuvres de Lavoisier, **2**, p. 715.

férentes saisons, dans différentes circonstances. On pourrait faire marcher ensemble des expériences correspondates par la combustion du phosphore. J'ai toujours eu le projet de me livrer à ces recherches, auxquelles j'étais naturellement conduit par les expériences que j'ai faites sur la salubrité de l'air des salles de spectacle et des dortoires des hôpitaux; mais je n'ai pu encore réaliser mon projet.

While Scheele first attempted a study of the effect of season and weather conditions on the oxygen content, we find Lavoisier emphasizing the importance of recognizing the influence of geographical locality upon the composition of the atmosphere.

Alkaline sulphides were used by Guyton[1] to absorb the oxygen quantitatively from the air; calcium sulphide was likewise employed by de Marti[2] in his analyses of the air of Catalonia. Upon comparing the different methods—nitric oxide, the Volta hydrogen eudiometer, phosphorus, moist iron and sulphur, and the alkaline sulphides—de Marti decided the last was the most satisfactory. The experiments were made during 1787, and his results are of especial interest, as they show his remarkable intuitiveness.

Among other refinements, de Marti recognized the importance of saturating his absorbing solution with nitrogen before use. He says regarding his researches:

The proof by sulphuret is that best calculated to ascertain the quantity of vital air contained in any gaseous fluid, since it will leave the mephitic air, and the other kinds of air which do not combine with it, without fear of any other gaseous substance being produced, or any lost, except the quantity of vital air, which alone has an affinity with the sulphuret, as I assured myself in 1787. A hundred parts of atmospheric air exposed to sulphuret lost between 0.21 and 0.23; and as several other proofs on the same air, made with nitrous gas, had taught me that it experienced no sensible variation, I was then convinced that the air which we breathe in Catalonia is constantly composed of from 0.21 to 0.23 of vital air, and from 0.77 to 0.79 of azotic gas. To ascertain whether there might not be variations afterwards in the proportion of these two principles which constitute in the atmosphere that elastic substance on which our life chiefly depends, I continued my experiments by means of sulphuret.

I repeated them so many times with atmospheric air, and on so great a number of days, that the uniformity in my results demonstrates not only the exactness of this method, but it seems to result from my observations made on the southern coast of this province:

1st, That the wind never caused the variation of a hundredth part in the respective quantities of vital air and azotic gas which compose the elastic fluid of our atmosphere, since I have always found that a hundred parts contained 79 of the latter and 21 of the former, without ever reaching 22.

2nd, That neither the moisture nor dryness of the atmosphere, nor the state of the latter in being more or less charged with exhalations, nor serene nor rainy weather, occasioned any difference.

3d, That the proportion of the quantities of the two same principles was equally constant during the days that Reaumur's thermometer stood at the freezing point, as well as during those when it indicated 24 degrees of heat.

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[1] Guyton, Chemisches Annalen, 1788, **1**, p. 316; *ibid*, 1796, **1**, p. 22.

[2] de Marti, Journal de Physique, 1801, **52**, p. 173; also printed in Philosophical Magazine, 1801, **9**, p. 250.

4th, That I did not observe any variation in the air thus taken while the mercury of the barometer was very low, and when it exceeded 28 inches.

In a word, during winter, in summer, in spring, and in autumn, in every month and at all hours, I found the air of my country, taken in the open fields, to be always composed of from 21 to 22 parts of vital air, and of from 78 to 79 of azotic gas.

But though this proportion does not vary a hundredth part in the course of several months, and even years, may it vary a very small part, such as a thousandth part, which after a very long time may become sufficiently sensible to make the proportion of the vital air of the atmosphere experience a progressive or periodical increase or diminution?

De Marti's researches, though carried out in 1787, were not translated into English until 1801, but his success with the sulphide of calcium evidently stimulated others to use the sulphides as reagents.

Berger[1] reports a series of experiments, using several forms of sulphide. With potassium sulphide, he found 21.65 per cent of oxygen; with iron sulphide, 21.19 per cent; with calcium sulphide, 20.88 per cent; and with sodium sulphide, 20.38 per cent. The agreement in these determinations led Berger to conclude that these eudiometric substances absorb from the air only one substance, namely, oxygen.

Henderson,[2] studying the changes which air undergoes as a result of respiratory processes, used "sulphuret of lime." On three days, June 16, 1803, June 18, 1803, and February 11, 1804, he analyzed common air and found 22 per cent of oxygen in all three cases.

Gay-Lussac,[3] using both the hydrogen eudiometer and the absorption by alkaline sulphides, made analyses of air collected in a balloon. He found with the hydrogen-explosion method that the air at a height of 6636 meters had the same composition as that on the surface of the earth, and that at both places they gave 21.49 per cent of oxygen. With the alkaline sulphide solution, he found 21.63 per cent in the air brought down in the balloon, and maintained that this slight increase over 21.49 per cent was inside the limit of error of the apparatus.

Julia de Fontanelle,[4] while making a tour of Europe, analyzed over 50 samples of air in France at the foot and summit of Canigou, with an elevation of 2780 meters, on the Corbiéres, on the Clape, and on the plains of Roussillon and Narbonne; also in Spain on the plains of Figueras, Gironne, and Barcelona, and on the mountains of St. Jerome-D' Ebron, Mont-Joui, etc. Using calcium sulphide, he found constantly 21 per cent of oxygen, with slightly more oxygen at noon than at midnight.

The last recorded use of the sulphide of calcium for air-analysis was made by Dalton,[5] who, however, gives no results, and by Moyle,[6] who analyzed the air of mines by this method in comparison with several others, including the long-discarded nitric-oxide method.

[1] Berger, Journal de Physique, 1802, 56, p. 375.
[2] Henderson, Nicholson's Journal, 1804, 8, p. 40.
[3] Gay-Lussac, Annales de Chimie, 1804, 52, p. 75.
[4] J.-S.-E.-Julia, Recherches historiques, chimiques et médicales sur l'air marécageaux, Paris, 1823.
[5] Dalton, Philosophical Magazine, 1838, 3d ser., 12, p. 158.
[6] Moyle, Annales de Chimie et de Physique, 1841, 3d ser., 3, p. 318.

With the passing of the nitric-oxide[1] and the alkaline-sulphide methods, we may consider the historical development of such methods as have survived a century or more of keen analytical criticism. Since this article has to deal primarily with the development of the knowledge regarding the composition of the outdoor air and but secondarily with methods, we may now advantageously consider the chronological records of progress in air-analysis.

In 1774, the brilliant Italian physicist, Volta,[2] announced his eudiometric method of employing the explosion of a confined volume of air with hydrogen by the electric spark. No results of his analyses are reported, but the process evidently attracted much attention, for we find that Cavendish,[3] while working on the composition of water, published the following interesting statements:

> From the fourth experiment it appears that 423 measures of inflammable air are nearly sufficient to completely phlogisticate 1000 of common air; and that the bulk of the air remaining after the explosion is then very little more than four-fifths of the common air employed; so that as common air can not be reduced to a much less bulk than that by any method of phlogistication, we may safely conclude, that when they are mixed in this proportion, and exploded, almost all the inflammable air, and about one-fifth part of the common air, lose their elasticity, and are condensed into the dew which lines the glass.

Although Cavendish was in no sense appreciative of the fact that this series of experiments proved the accuracy of the Volta eudiometer for air-analysis, the results are surprisingly accurate.

Shortly afterwards the method was adversely criticized by Seguin,[4] who maintained that the apparatus gave only comparative results and could never be taken as an absolute measure, and by Berthollet,[5] who objected to the complicated apparatus. The latter remarked on the probable contamination of the hydrogen by carbonaceous gases and pointed out that we do not as yet know enough about the specific weight of the two different gases. But in spite of this adverse criticism, the method was most carefully employed in analyzing samples of air brought from a great height by Gay-Lussac in a balloon flight.[6] Later, von Humboldt and Gay-Lussac[7] published a long research with the Volta eudiometer on the composition of air taken over the Seine under varying weather

[1] It is interesting to note that in 1890 Wanklyn and Cooper resurrected the nitric-oxide method and enthusiastically recommended its use, reporting three analyses of pure air as giving 20.59, 20.54, and 20.67 per cent of oxygen respectively. Chemists have not accepted the method for modern use. (See Wanklyn and Cooper, Air-analysis, London, 1890, p. 35.)

[2] Volta, Sopra Un Nova Eudiometro. Lettera al Signor Dottore Giuseppe Priestley, Como, 2 Settembre, 1777. Published in Collezione dell'Opere. del Cavaliere Conte Alessandro Volta, Firenze, 1816, 3, p. 177. Originally published, Scelta di Opuscoli interessanti di Milano, 1777, 34, p. 65.

[3] Cavendish, Philosophical Transactions, 1784, 74, pp. 119–153.

[4] Seguin, Annales de Chimie, 1791, 9, p. 293.

[5] Berthollet, Memoires sur l'Egypt publiés pendant les Campagnes du Général Bonaparte. Paris, 1800 (Année 8), p. 284.

[6] Gay-Lussac, Annales de Chimie, 1805, **52**, p. 75.

[7] v. Humboldt and Gay-Lussac, Journal de Physique, **60**, p. 129.

conditions. Although in the analyses of air collected by Gay-Lussac in the balloon, the ratio of hydrogen to oxygen was erroneously taken as 2.04 to 1, von Humboldt and Gay-Lussac used in this research the correct ratio, 2 to 1, which had but recently been established. In this paper von Humboldt acknowledges his error in advocating so strongly the nitric-oxide eudiometer in his contention with Berthollet a few years before.

The analyses of the air were made on the day of collection, a summary of the results being given.

TABLE 1.—*Results of a research on the composition of air, made with the Volta eudiometer, by Humboldt and Gay-Lussac.*

Date.	Temperature.	Weather conditions.	Wind.	Oxygen.
1804	°*C.*			*p. ct.*
Nov. 17	7.3	Overcast	E.	21.0
				21.0
Nov. 18	4.5	....Do.	ESE.	21.0
				21.0
Nov. 19	4.7	Fine rain	Very strong, SW. to W.	21.0
				21.0
Nov. 20	10.0	....Do.	S.	21.0
				21.1
Nov. 21	12.5	Overcast	SW.	21.2
				21.0
Nov. 22	6.7	Cloudy; little rain	SW.	21.0
				21.0
Nov. 23	1.5	Cloudy	W.	21.0
				21.0
Nov. 24	8.5	Rain	S.	21.0
				21.1
Nov. 25	10.6	Overcast	SW.	21.0
				21.1
Nov. 26	3.3	Cloudy	E.	21.1
				21.0
Nov. 27	1.6	Frost	N.	21.1
Nov. 28	1.3	Snow	N.	21.0
Dec. 1	4.1	Fog	NNE.	21.0
Dec. 3	2.3	Cloudy	E.	20.9
Dec. 5	4.2	Rain	S.	21.0
Dec. 7	3.1	Thick Fog		21.0
Dec. 13	9.6	Rain	SSW.	21.0
Dec. 19	2.2	Overcast	NE.	21.0
Dec. 23	1.0	Heavy frost; thick fog.	SE.	21.0

The authors conclude that they have shown, first, that the atmospheric air does not vary in composition; second, that there are 21 parts of oxygen in 100 parts of air; third, that there are no noticeable amounts of hydrogen present in the air. This investigation is the first extensive research into the composition of the atmosphere employing the hydrogen eudiometer, and the conclusions drawn by the authors are astonishingly correct when it is considered that the research was carried out over a century ago. That the errors in the apparatus were far greater than are permissible in modern research, especially when such fundamental deductions are to be made, should not in any way dim the brilliancy of the work of these investigators. Subsequently, the method was to have exten-

sive use, be considerably increased in accuracy, and contribute materially to our knowledge of the oxygen content of the air.

Henry[1] analyzed atmospheric air frequently, using the Volta eudiometer. He reports that he was unable to satisfy himself "whether it contains 21 or 20 volumes of oxygen in 100, the proportion being mostly between these two extremes."

Simultaneously with the Volta eudiometer, another method of air-analysis was rapidly developed, which was also based upon the fundamental observations of Scheele with regard to the absorption of oxygen from a confined volume of air by slowly or rapidly burning phosphorus. Scheele's experiments have already been cited, but in the English translation of his book,[2] we find Richard Kirwan criticizing adversely Scheele's results, maintaining that Lavoisier, when using the combustion of phosphorus, never found more than between one-fifth and one-sixth of oxygen absorbed, while Scheele, it will be remembered, found a much larger contraction in volume. Kirwan also pointed out that Fontana had made experiments with phosphorus but found the diminution in volume much less than that found by Scheele. Later Lavoisier[3] mentioned the fact that when employing the combustion of phosphorus he found the quantity of vital air contained in the atmosphere was about 27.5 parts in 100.

Volta, in a letter to Priestley,[4] wrote in a general way of his experience with "Bolognian phosphorus," showing that at the same time Scheele in Sweden, Lavoisier in Paris, and Volta in Italy were using phosphorus to absorb oxygen from the air. Rapidly burning phosphorus was also employed by Achard,[5] who described two eudiometers, one for nitric oxide and one for rapidly burning phosphorus.

Dissatisfied with the incomplete descriptions and development of the earlier methods employing ignited phosphorus, Seguin[6] in his memoir on eudiometry described accurately the methods used by Lavoisier and himself, but gave no results. It is noteworthy that after the ignition of the phosphorus and the contraction in the volume of the air, they placed in the jar a little caustic alkali to absorb the carbon dioxide and the phosphoric acid. Seguin maintained that this method was very rapid and very exact.

Simultaneously with his condemnation of the nitric-oxide eudiometer, Berthollet advocated the use of slow-burning phosphorus.[7] In his observations on eudiometry, he criticized severely the nitric-oxide eudiometer and the Volta hydrogen eudiometer, and stated that the use of alkaline sulphide is too long a process and that hydrogen sulphide is present.

[1] Henry, Elements of experimental chemistry, London, 1829, 11th ed., **1**, p. 316.
[2] Scheele, Experiments on air and fire, London, 1780, p. 202.
[3] Lavoisier, Memoires de l'Academie des Sciences, 1782, p. 486; also in Oeuvres de Lavoisier, 1862, **2**, p. 503.
[4] Priestley, loc. cit., 1777, **3**, p. 381.
[5] Achard, Nouveaux Memoire de l'Academie Royale des Sciences et Belles Lettres, for the year 1778 (published 1780), p. 91.
[6] Seguin, Annales de Chimie, 1791, **9**, p. 293.
[7] Berthollet, Memoires sur l'Egypt publiés pendant les Campagnes du Général Bonaparte. Paris, 1800, (Année 8), p. 284.

Berthollet's expressions regarding the existing condition of air-analysis methods is of special interest even at the present day:

Depuis que l'on sait que l'air atmosphérique est composé de gaz oxygène et de gaz azote, on a cherché à déterminer les proportions de ces deux gaz, et les variations que peuvent y survenir; mais on n'est point encore d'accord sur la méthode qu'on doit préférer, et sur le résultat auquel on doit s'arrêter.

Believing the use of slow-burning phosphorus to be the best method, he passed a cylindrical stick of phosphorus into air collected over water in a glass vessel. At the ordinary temperature of Cairo it required about 2 hours for complete absorption, but in Paris he found it required 6 to 8 hours. A correction of one-fortieth for phosphorus vapor was recommended. In Cairo he found that the air contained generally 22 parts of oxygen, with a variation of hardly more than 0.5 part. A most interesting discussion of the factors affecting the composition of the atmosphere concludes his paper:

En effet, comment peut-on concevoir que l'atmosphère continuellement agitée par des mouvements qui la transportent rapidement, qui changent ses contacts et la renouvellent, puisse varier considérablement d'un village à un autre: il y a cependant une exception à faire pour les lieux qui sont fort élevés audessus du niveau de la mer. La différence de pesanteur spécifique entre le gaz oxygène et le gaz azote, qui, dans l'etat élastique, n'exercent réciproquement qu'une très faible action, explique celle qui a été trouvée dans leurs proportions.

Parrot in Riga began active experimenting in phosphorus eudiometry in the latter part of 1799, and in 1800 described an apparatus which he called an oxygenometer.[1] In a letter to Gilbert[2] he emphasized the importance of temperature changes, noting that a change of 4° or 5° Reaumur may produce a change of 1 to 2 per cent in the oxygen measurement. In his later experiments he found that the oxygen varied from 20.7 to 23 per cent. By applying a correction—not identical, however, with Berthollet's one-fortieth—the results were 22.25 and 24.72 per cent by volume. He concluded that the greatest variation was 2.5 per cent and that the greatest oxygen content of the air was about 25 per cent. His arguments for variation in the oxygen content of the atmosphere are of interest:

Der Grund, den Berthollet für die Beständigkeit des Sauerstoffgehalts angiebt, nämlich die Bewegung der Luft, beweist allerdings, dass dieser Gehalt nicht sehr stark variieren kann, schliest aber Variationen von 2 bis 2½ pC. nicht aus, es versteht sich, für sehr entfernte Orte und verschiedne Zeiten. Ein Wind, der 15 Fuss in einer Sekunde durchläuft, braucht etwa 5 Tage, um eine Strecke von 18° zu durchstreichen. Warum sollte z. B. vor einem Südwinde die Luft in Schottland, Schweden, Norwegen, Russland nicht an Sauerstoff ärmer seyn, als 5 Tage nach dessen Entstehung, wenn z. B. eine üppige Vegetation, von vielem Sonnenscheine begünstigt, viel Sauerstoffgas in Italien, im nördlichen Afrika, in Griechenland entwickelt hat? Warum sollte ein Ostwind, der über Asiens Vegetation herkömmt, nicht Europa mit mehr Sauerstoff versehen, als der Westwind, der über das atlantische Meer herweht, wo er keine Sauerstoff-Entwickelung antrifft?

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[1] Parrot, Voigt's Magazine, 1800, **2**, p. 154.
[2] Parrot, Gilbert's Annalen der Physik, 1802, **10**, p. 193.

F. Berger[1] in Geneva, in a paper criticizing the Fontana eudiometer, mentions the phosphorus eudiometer as "introduced" by Giobert[2] of Turin and "improved" by Spallanzani.[3] A number of tests comparing the nitric-oxide with the phosphorus eudiometer all show the great advantage of the latter. Using both alkaline sulphides and the phosphorus eudiometer, he always found between 20 and 21 per cent. He analyzed air from the glacier of Mont Cervin and other glaciers, but found the air over the glacier no purer than air from the same height on a mountain. He concludes that the atmosphere is throughout the whole extent of equal composition and that the oxygen is very nearly one-fifth of the total air.

The activity of numerous chemists in advocating various methods for absorbing oxygen led to the rapid accumulation of evidence in favor of the phosphorus and hydrogen eudiometers, but the latter seemed to have the most extended use.

Biot,[4] during a study of the air contained in the bladders of fishes, analyzed the air of two islands in the Mediterranean, Formentera and Iviza. They report that the analyses, which were made by the hydrogen-explosion method, showed consistently an oxygen content of 21 per cent.

In a like research, *i.e.*, the analysis of the air contained in the bladders of fishes, Configliachi[5] used side by side the phosphorus and the hydrogen eudiometers, but apparently was more confident of results obtained with the latter. In this research, analyses were made of outdoor air from mountains, marshes, and grain fields. He concludes that his results, which are given in table 2, show the uniform composition of the atmosphere.

TABLE 2.—*Comparative study of the percentage of oxygen in atmospheric air, made by Configliachi.*

Mountain air.		Air of lowlands.	
		Grain field.	Marsh.
	p. ct.	*p. ct.*	*p. ct.*
Pizzo Legnone (2642 meters)...	21.0	20.9	21.0
St. Bernard (472 meters)	21.1	20.8	20.9
		20.8	21.0
Mont Cenis (2067 meters)	21.0	20.7	21.0
		20.6	20.9
Simplon (2006 meters)	20.9	20.8	21.9

Employing a phosphorus eudiometer, Vogel[6] found in the air from the Baltic Sea between 20 and 21 per cent of oxygen, the latter figure never

[1] Berger, Journal de Physique, 1802, **56**, p. 253.
[2] Giobert (Journal de Physique, 1798, **47**, p. 197) analyzed the air of Vaudier and of Turin by the combustion of phosphorus. This refers probably to rapid rather than slow combustion. In Vaudier he found from 25 to 33 per cent of oxygen, but in Turin the variation was much less, being 26 to 28 per cent.
[3] Spallanzani, in his Memoires sur la Respiration, Geneva, 1803, p. 101, states that the air we breathe contains 27 per cent of oxygen.
[4] Biot, Gilbert's Annalen der Physik, 1807, **26**, p. 459.
[5] Configliachi, Journal für Chemie und Physik, 1811, **1**, p. 137.
[6] Vogel, Gilbert's Annalen der Physik und der physikalischen Chemie, 1820, **6**, p. 93.

being attained. Kruger reported to Vogel the result of four analyses, made with a Volta eudiometer, of sea-air taken on a half mile from shore, in which he never found over 20.59 per cent of oxygen. The author's explanation of this low figure is that the oxygen had been absorbed by the water.

Another investigation of air from the Baltic Sea was made by Hermbstädt[1] in 1821. Although his method of sampling is questionable, he asserts that he employed a "very exact" Volta eudiometer. Air taken 5 feet above the surface of the sea gave 21.5 per cent of oxygen; air 16 feet above the sea, 20.5 per cent; and air 24 feet inland from the shore, exactly 20 per cent. The author concludes that the larger oxygen content of air from the sea is due to the continuous evolution of oxygen from either the sea-water or marine life.

Thomson,[2] in Edinburgh, was occupied in air-analysis many years and, indeed, states that in 1801 he made experiments which showed that the composition of the air in Edinburgh was the same as that found by Davy and Berthollet elsewhere. In 1824 he made a new series of tests, employing the Volta eudiometer. After much experimenting as to the proper volume of hydrogen to use, he found, as the average of 10 experiments, 79.9335 per cent of nitrogen and 20.0665 per cent of oxygen. Thomson's analyses and conclusions are so obviously dominated by the preconceived notion that air is a chemical compound consisting of four parts of nitrogen and one of oxygen, that his contribution has very little quantitative interest.

Another Englishman, John Dalton, whose theoretical discussions were of great importance to chemists, also analyzed air upon a number of occasions. On January 8, 1825,[3] he found as a result of many experiments, 21.15 per cent of oxygen in air sampled in the country, the barometer being 30.9 inches, and the wind blowing very moderately from the north-east after 3 days of calm and a light frost. He states that ordinarily the atmosphere has only 20.7 to 20.8 per cent of oxygen. Dalton's conception of the independent nature of each gas and the computed differences in composition of the air at different heights greatly stimulated research in this direction. In contradiction of his expressed views upon the solubility of gases in water, he collected samples by letting the water run out of a bottle and then corking the bottle. Frequently it was opened under water and allowed to stand several months. In the Philosophical Magazine, 1838, **12**, p. 397, Dalton gives further experimental evidence to support his view, but is evidently convinced that the theoretical computations are not verified by experiment. Thus he states:

From the experiments about to be related, I have reason to believe that the higher regions of the atmosphere are somewhat less abundant in the proportion of oxygen than

[1] Hermbstädt, Journal für Chemie und Physik, 1821, **32**, p. 283.
[2] Records of general science, by Robert D. Thomson, M.D., 1836, **15**, p. 179. See also Journal für praktische Chemie, 1836, **8**, p. 359.
[3] Dalton, Annals of Philosophy, 1825, **10**, p. 304.

the lower, though the reverse might be expected from the enormous consumption of oxygen by daily processes on the surface of the earth, when we know of no proportionate consumption of azote. It appears, however, that the disproportion of the two elements at different elevations is by no means so great as theory requires; and therefore we must conclude the unceasing agitation of the atmosphere by currents and counter-currents is sufficient to maintain an almost uniform mixture at the different elevations to which we have access.

His experimental evidence consists of analyses of samples from Mount Helvellyn (3000 feet), Snowdon (3570 feet), two balloon journeys made by Green at 9600 feet and 15,000 feet respectively, and three samples from Switzerland sent by Crewdson from Mer de Glace, the Simplon Pass, and the Wengern Alps. The results, together with an abstract of the many analyses of Manchester air made for comparison, are given in table 4.

Referring to the results obtained from these analyses, Dalton says:

The general conclusions, it seems to me, to be drawn from these experiments are, that the proportion of oxygen to azote in the atmosphere on the surface of the earth is not precisely the same at all places and times; and that in elevated regions the proportion of oxygen to azote is somewhat less than at the surface of the earth, but not nearly so much so as the theory of mixed gases would require; and that the reason for this last must be found in the incessant agitation in the atmosphere from winds and other causes.

Numerous computations as to the composition of the atmosphere in higher strata, based upon Dalton's hypotheses, have been made from time to time by Babinet,[1] Benzenberg,[2] Bauer,[3] Morley,[4] and Hinrichs.[5] The values computed by Morley and Hinrichs are given in table 3.

TABLE 3.—*Percentages of oxygen in high-strata air, as computed by Morley and Hinrichs.*

Height.	Oxygen.		Height.	Oxygen.	
	Morley.	Hinrichs.		Morley.	Hinrichs.
kilometers.	*p. ct.*	*p. ct.*	*kilometers.*	*p. ct.*	*p. ct.*
0	20.96	21.00	10	18.31	18.43
1	20.68	....	20	15.92	16.07
2	20.41	....	30	....	13.90
3	20.14	....	40	....	11.86
4	19.87	....	50	10.25	9.83
5	19.60	....	60	....	7.52
6	19.34	....	70	....	4.7
7	19.07	....	80	....	2.2
8	18.82	....	90	....	0.7
9	18.56	....	100	4.69	0.3

[1] Cited by Dumas and Boussingault, Annales de Chimie et Physique, 1841, 3d ser., **3**, p. 258.
[2] Benzenberg, Poggendorff's Annalen der Physik und Chemie, 1834, **31**, p. 8.
[3] Bauer, Poggendorff's Annalen der Physik und Chemie, 1868, **135**, p. 135; also Zeitschrift für analytische Chemie, 1869, **8**, p. 397.
[4] Morley, The American Journal of Science, 1879, 3d ser., **18**, p. 168.
[5] Hinrichs, Comptes rendus, 1900, **131**, p. 442.

TABLE 4.—*Percentages of oxygen in analyses of air made by Dalton.*

Date.	No. of experiments averaged.	Barometer.	Weather.	Place.	Oxygen.
1824					*p. ct.*
July 14	4	....	....	Summit of Helvellyn (3000 ft.).	20.70
July 14	4	....	....	Manchester..........	20.88
Nov. 23	6	28.0	Rain; wind SE., strong.	Town air............	20.25
1825					
Jan. 8	4	30.94	Following a week of calm weather.	....Do.	21.12
June 8	4	29.90	....	....Do.	20.97
June 10	6	30.30	Sunny and sultry; wind SW.	Field near the town ...	20.58
Nov. 3	10	28.76	Rainy; wind SW.....	Town air............	20.6
1826					
May 14[1]	10	26.20	Wind NE., light	Summit of Snowdon, 3570 ft. above the sea.	20.65
May 14	6	....	....	Country, 3 miles from Manchester.	20.8
May 18[2]	6	....	Wind SW., light	Summit of Snowdon...	20.59
May 18[2]	4	....	....	Second bottle from Snowdon.	20.9
May 18	....	....	....	Country, near Manchester	20.7
May 18	5	....	....	Town air	21.04
July	10	....	....	Summit of Helvellyn ..	20.63
				Town air............	20.73
1827					
June 27[3]	7	....	....	Balloon voyage over Cheshire (9600 ft.).	20.7
June 27	7	....	....	Town air............	20.83
July 2	8	....	....	....Do.	20.8
1828					
Aug. 5	13	....	....	Town air............	20.92
Aug. 5	2	....	....	Summit of Snowdon ..	20.44
1831					
July 4[4]	....	....	Rain and fog; wind SW.	Summit of Helvellyn ..	20.57
1832					
July 26	5	16.8	....	Collected from balloon; altitude, 15,000 ft. (first phial).	20.59
July 27	5	....	....	Town air............	20.95
1835					
Aug. 21[5]	4	....	....	Mer de Glace, 6000 ft. above the sea.	20.2
Aug. 21[5]	[6]4	....	....		19.4
Aug. 29[5]	4	....	....	Simplon Pass, 6174 ft.	19.98
Aug. 29[5]	[6]4	....	....		19.53
Sept. 15[5]	4	....	....	Wengern Alps, 6230 ft.	20.45
Sept. 15[5]	[6]4	....	....		20.11

[1] Analyzed on May 28, 1826.
[2] Analyzed on May 25, 1826.
[3] Collected on June 26, 1827.
[4] Analyzed on July 21, 1831, or 17 days later.
[5] All analyzed in October, 1835.
[6] Duplicate.

The explosion of hydrogen and air by the electric spark, as originally proposed by Volta, had been the only method of uniting hydrogen and oxygen in gas-analysis up to 1824, when Doebereiner[1] announced his discovery of the catalytic action of platinum sponge.

[1] Doebereiner, Schweiggers Journal für Chemie und Physik, 1824, **42**, p. 60.

On a trip to South America in 1825, Boussingault[1] made observations on the oxygen content of the air at various altitudes. In at least one analysis he used platinum sponge, for he reports that air taken in November, 1826, at Mariquita, in the valley of the Magdalena, at an altitude of 548 meters, gave with platinum sponge 20.77 per cent of oxygen.

Two analyses made with the Volta eudiometer gave results as follows:

December 1826, Ibagué (1323 meters) .... 20.7 per cent.
April 1825, Santa Fé de Bogota (2643 meters) .... 20.65 per cent.

Boussingault concluded that his observations were not in accord with the Dalton hypothesis.

Turner,[2] in a paper read before the Royal Society of Edinburgh, 1824, reported his experiences with the use of spongy platinum on a mixture of air and hydrogen. Three experiments gave 21.8, 22.3, and 21.7 per cent of oxygen, respectively. Suspecting the purity of his hydrogen, he left an active ball of spongy platinum in contact with hydrogen over night and made 6 tests the next day. The results were 20.3, 20.3, 20.7, 21, 21.3, and 21.7 per cent of oxygen, respectively, the mean of these experiments being 20.88 per cent; he assumes 21 per cent of oxygen as the correct value.

TABLE 5.—*Percentages of oxygen obtained by Baumgartner in atmospheric air.*

Date.	Oxygen.	Date.	Oxygen.	Date.	Oxygen.
1831	*p. ct.*	1831	*p. ct.*	1831	*p. ct.*
Sept. 24	20.6	Oct. 4	21.1	Oct. 14	21.0
Sept. 25	21.4	Oct. 5	21.4	Oct. 15	20.9
Sept. 26	21.0	Oct. 6	21.3	Oct. 16	20.7
Sept. 27	20.9	Oct. 7	21.1	Oct. 17	21.0
Sept. 28	21.1	Oct. 8	20.9	Oct. 18	20.7
Sept. 29	21.2	Oct. 9	20.9	Oct. 19	20.8
Sept. 30	21.2	Oct. 10	20.9	Oct. 20	21.0
Oct. 1	21.4	Oct. 11	21.0	Oct. 21	21.0
Oct. 2	20.4	Oct. 12	20.7	Oct. 22	21.0
Oct. 3	21.3	Oct. 13	20.8		

Degen[3] in Stuttgart likewise used platinum sponge and found in outdoor air 20.80, 20.88, and 20.89 per cent.

Kupffer[4] in Kasan, by using a Volta eudiometer and mixing 99 parts of hydrogen with 198 parts of air, found after explosion a residue of 171 to 172 parts, corresponding to 21 to 21.2 per cent of oxygen.

The appearance of cholera in Vienna in 1831 led to an exhaustive study of the atmosphere by Baumgartner,[5] who analyzed the air each day from September 24, 1831, to January 31, 1832, by means of the Volta eudiometer. Differences between analyses on the same sample seldom varied 0.2 per cent.

[1] Boussingault, Annales de Chimie et de Physique, 1841, 3rd ser., **1**, p. 354.
[2] Turner, abstracted in Boston Journal of Philosophy, 1825, **2**, p. 238.
[3] Degen, Poggendorff's Annalen der Physik and Chemie, 1833, **27**, p. 557.
[4] Kupffer, Annales de Chimie et de Physique, 1829, **41**, p. 423.
[5] Baumgartner, Medicinische Jahrbücher des k. k. österreichischen Staates, 1832, **12**, p. 83.

The results for the first month, which are fairly representative of the remainder of the study, are given in table 5.

The use of a metal to absorb oxygen was first suggested by Scheele,[1] who employed metallic iron. A Spaniard, Luzuriaga,[2] in 1784, used lead, but his results are not available.

The first practical use of a metal as an oxygen absorbent in air-analysis was made by Theod. de Saussure,[3] who employed lead shavings moistened with a very little water. After shaking them 3 hours, he found that the absorption was complete. de Saussure criticized the earlier methods, since so many divergent results were obtained by different workers, considering the Volta eudiometer especially open to criticism, as there was always danger of an impurity in the hydrogen. He believed the lead method, though not so convenient, to be much more accurate. A statement of his results is given in table 6.

TABLE 6.—*Results obtained by de Saussure with the lead method.*

Place.	Date.	Weather.	Oxygen and carbon dioxide absorbed.
			p. ct.
Lake of Geneva	July 18	Quiet and clear	21.08
Chambeisy[1]	Aug. 3	Clear; NE. wind	20.98
Do.	Aug. 16	Clear; light SW. wind	21.03
Street in Geneva	Aug. 25	Clear; light NE. wind	21.03
Chambeisy	Aug. 27	Rainy; strong SW. wind	21.13
Do.	Aug. 27	....Do.	21.15
Do.	Sept. 13	Clear; light NE. wind	21.08
Lake of Geneva	Sept. 13	....Do.	21.09
Chambeisy	Nov. 5	Overcast; calm	20.98
Do.	Nov. 21	Overcast; strong NE. wind	21.086
Do.	Dec. 13	Quiet; foggy	21.006
Do.	Dec. 24	Overcast; strong NE. wind	21.1
Do.	Dec. 28	Clear; strong NE. wind	21.0
Lake of Geneva	Dec. 29	Partly overcast; light SW. wind	21.04
Average of all			21.05
Carbon dioxide			.04
Oxygen in 100 parts of air			21.01

[1] Meadow 1 league from Geneva.

From these results one concludes that de Saussure determined carbon dioxide and oxygen together and subsequently deducted the carbon dioxide. His results show surprising constancy in the oxygen content of the air.

Dupasquier,[4] employing the alkaline ferrous hydroxide originally employed by Scheele, found that normal air always gave 21 per cent. Somewhat later, Brunner[5] reverted to the precipitated ferrous hydroxide method, but reported no air-analyses.

[1] Scheele, Air and Fire, London, 1780, p. 13.
[2] See Kopp's Geschichte der Chemie, 1845, **3**, p. 211.
[3] de Saussure, Annalen der Physik, 1836, ser. 2, **8**, p. 171.
[4] Dupasquier, Annales de Chimie et de Physique, 1843, 3d ser., **9**, p. 247.
[5] Brunner, Poggendorff's Annalen der Physik und Chemie, 1848, Ergänzungsband, **2**, p. 509.

THE FOUNDATIONS OF MODERN AIR-ANALYSIS.

About 1840, Bunsen in Marburg, working with that marvelous technique that characterized all of his chemical observations, developed to the highest degree the explosion method with hydrogen for determining oxygen. A preliminary description of much of his technique was published in an article by Kolbe.[1] Bunsen's apparatus is there described and to demonstrate the accuracy of the apparatus several analyses of atmospheric air were made in 1846. These analyses with slightly corrected figures are given again in detail in Bunsen's book,[2] and are reproduced in table 7.

Bunsen expressed the belief that the composition of the air could be determined much more accurately if the eudiometer readings were repeated from hour to hour. One such analysis made on May 31, 1847, gave 20.964 per cent.

TABLE 7.—*Results obtained by Bunsen with the hydrogen-explosion method.*

Date.	Oxygen.	Date.	Oxygen.	Date.	Oxygen.
1846	*p. ct.*	1846	*p. ct.*	1846	*p. ct.*
Jan. 9	20.970 20.963	Jan. 22	20.919 20.880	Feb. 1	20.840 20.859
Jan. 11	20.927	Jan. 24	20.921 20.943	Feb. 3	20.925 20.940
Jan. 13	20.914	Jan. 26	20.927 20.934	Feb. 5	20.937 20.952
Jan. 14	20.950 With another eudiometer	Jan. 28	20.928 20.911	Feb. 8	20.953
Jan. 18	20.906 20.928	Jan. 30	20.889 20.892		
Jan. 20	20.927 20.927				

These figures of Bunsen marked a great advance in accuracy, and it is important to note that Bunsen's method subsequently received extensive use by different investigators. An extract from a letter written by Bunsen to J. J. Berzelius on November 3, 1846, is of especial interest in connection with the main problem of this memoir.[3]

> Ich habe zunächst meine Aufmerksamkeit auf einige Fragen über die Zusammensetzung der atmosphärischen Luft gerichtet und befinde mich im Besitz von mehr als 300 gleichzeitig in Marburg, Copenhagen, Reykjavik, in der Nähe des Polarkreises und auf dem atlantischen Ocean aufgefanger, und in zugeschmolzenen Glasgefässen bewahrter Luft proben, die zu Analysen nach einer Methode ausreichen, deren Schärfe und Sicherheit kaum etwas zu wünschen übrig lässt, wie die nachstehenden zur Prüfung dieser methode in verflossenen Winter angestellten Versuche beweisen.

[1] Kolbe, "Eudiometer, Eudiometrie" in the Handwörterbuch der Chemie, Liebig, Poggendorff and Wöhler, 1842, **2**, p. 1050.
[2] Bunsen, Gasometrische Methoden, Braunschweig, 1857, p. 77.
[3] Gesammelte Abhandlungen von R. Bunsen, Leipzig, 1904, **2**, p. 4.

Unfortunately nowhere in Bunsen's subsequent publications do we find any record of the analyses of this large number of samples of air, and obviously the pressure of other work prevented his carrying out this inquiry. It is greatly to be regretted that with his masterful technique such analyses could not have been made.

Although Lavoisier had shown that when phosphorus was burned in air there was an increase in weight corresponding to the diminution in volume of the air, nevertheless no air-analyses were based upon gravimetric determinations until the appearance in 1833 and 1834 of the unique method of Brunner[1] in Berne. Brunner devised a plan of passing a volume of air through a tube that contained some suitable absorbent for oxygen which could be weighed. All previous determinations had been made over water, or occasionally mercury, upon relatively small volumes of air confined in glass tubes, eudiometers, etc., but with Brunner's method, a considerably larger volume of air could be used. Furthermore, it was possible by this process to measure likewise the amount of nitrogen remaining in the gas, and thus make a determination not only of oxygen by weight, but of nitrogen by volume. After a number of preliminary experiments made with iron and with copper, Brunner finally decided upon phosphorus as the best absorbent. With perfectly dry phosphorus and a very moderate air-current, he found that oxygen was rapidly and quantitatively absorbed.

In 1833 Brunner made a series of experiments in Berne in which he determined the average oxygen content of the air as 21.0705 per cent. The agreement was usually within 0.1 per cent, although occasionally the variation was as high as 0.2 per cent. Of interest, also, is the fact that he analyzed air taken on the Faulhorn on July 18, 19, and 20 of the same year; from 14 determinations he found the oxygen varying from 20.75 to 21.11 per cent, the average of all being 20.915. Eight years later, in July 1841,[2] Brunner made 7 experiments in the same manner as those made at Berne, and found ranges from 20.75 to 20.867 per cent, with an average of 20.821 per cent. The fact that this latter value is very much less than those found 8 years before is explained by Brunner on the ground that there was probably an error in the measurement of the size of the vessel used in the earlier experiments. Brunner's article is particularly valuable, as it contains a critical discussion of methods and of the limit of accuracy of the various methods that had been proposed for absorbing oxygen.

While Brunner had successfully weighed the oxygen absorbed from the air, he had always measured the volume of nitrogen. In 1841 Dumas and Boussingault[3] published a research which in plan was quite similar to that of Brunner, except that they not only weighed the oxygen but like-

[1] Brunner, Poggendorff's Annalen der Physik und Chemie, 1833, ser. 2, **27**, p. 1; also, *ibid.*, 1834, ser. 2, **31**, p. 1.
[2] Brunner, Annales de Chimie et de Physique, ser. 3, 1841, **3**, p. 305.
[3] Dumas and Boussingault, Annales de Chimie et de Physique, ser. 3, 1841, **3**, p. 257.

wise the nitrogen. By using large glass vessels which could be evacuated and passing the air over heated metallic copper, they absorbed the oxygen by the copper, weighing the vessel before and after absorption, thus giving a true weight of the nitrogen left behind. The method was obviously best used by its illustrious devisers, since it was much more technical and difficult to carry out than any previously suggested. By means of two apparatus, simultaneous experiments were made in 1841. The percentage volumes of oxygen found are given in table 8. These samples were all taken during very clear and beautiful weather, and as a control a sample was taken on May 29, 1841, during rain. The result was essentially that found during the clear weather, viz, 20.817 per cent of oxygen.

TABLE 8.—*Percentages of oxygen in air analyzed by Dumas and Boussingault.*

Date.	First analysis.	Second analysis.	Average.
1841	*p. ct.*	*p. ct.*	*p. ct.*
Apr. 27	20.73	20.73	20.73
Apr. 28	20.83	20.88	20.86
Apr. 29	20.83	20.84	20.83
Average ..	20.80	20.82	20.81

Although the experimental evidence of Gay-Lussac and von Humboldt, as well as the earlier observations of Boussingault in South America, agreed perfectly with the more recent work of Dumas and Boussingault, nevertheless, owing to the importance of the Dalton hypothesis, Dumas and Boussingault decided upon making some analyses of air taken from the Faulhorn. By previous arrangement with Brunner in Berne, a series of experiments was planned in which samples of air would be taken simultaneously in Paris, Berne, and on the Faulhorn. These latter were collected by means of large evacuated glass balloons which were sent by Dumas from Paris. In Berne, Brunner operated with his method previously described. The results of these comparisons, which represent the first coöperative investigation of any magnitude on the composition of the air, are given in table 9.

TABLE 9.—*Percentages of oxygen in air analyzed by Dumas and Boussingault, and by Brunner.*

Date.	Paris.	Faulhorn.	Berne.
	p. ct.	*p. ct.*	*p. ct.*
July 20	20.85	20.77	20.80
July 21	20.80	20.89	20.70
July 24	20.87	{ 20.76 20.67	20.78 20.77
Aug. 7		20.78	
Average ..	20.84	20.78	20.76

While there is a difference between the samples in Paris and the samples in Berne and on the Faulhorn, it is important to note that somewhat

later some 50-liter samples, which were taken in Paris and analyzed with the very greatest care, showed variations equally as great; thus, on September 20 the percentage was 20.875, while on September 22 it was 20.709.

Brunner's method was used successfully by Verver[1] in Gröningen in May and August 1838. As a result of 45 analyses, he found the average oxygen content of carbon-dioxide and water-free air to be 20.864 per cent. The oxygen percentages obtained by Verver are given in table 10.

TABLE 10.—*Percentages of oxygen in air analyzed by Verver.*

Date.	Oxygen.	Date.	Oxygen.	Date.	Oxygen.
1838.	*p. ct.*	1838.	*p. ct.*	1838.	*p. ct.*
May 21	21.00	May 24	21.09	Aug. 2	20.96
May 21	20.70	May 24	20.88	Aug. 3	20.70
May 21	20.80	May 24	20.76	Aug. 3	20.80
May 21	20.85	May 25	21.10	Aug. 3	21.05
May 22	20.79	May 25	21.06	Aug. 3	20.90
May 22	21.00	May 25	21.02	Aug. 3	20.80
May 22	20.77	May 25	21.06	Aug. 5	20.60
May 22	20.95	Aug. 1	20.90	Aug. 5	20.70
May 23	20.93	Aug. 1	21.08	Aug. 5	20.65
May 23	20.91	Aug. 1	20.90	Aug. 5	20.64
May 23	20.85	Aug. 2	20.91	Aug. 5	20.90
May 23	20.90	Aug. 2	20.80	Aug. 5	20.90
May 23	20.94	Aug. 2	20.80	Aug. 6	20.70
May 24	20.82	Aug. 2	20.90	Aug. 6	20.70
May 24	20.67	Aug. 2	20.80	Aug. 6	20.70

Dumas and Boussingault were at first inclined to believe that since their results, those of Berger, Gay-Lussac, and von Humboldt, the earlier results of Boussingault, and the results of Brunner, all agreed so remarkably, the composition of the atmosphere was uniform. Subsequent experiments made in combination with Brunner on the air from the Faulhorn, Paris, and Berne showed that there were also differences; they accordingly modified their conception and said that although on the whole the composition of the air was constant, nevertheless there must be certain variations which might occur.

The demonstrated accuracy of the method of Dumas and Boussingault led to its extensive use by other observers. In 1841 and 1842 Lewy made analyses of air from the North Sea, the court of the Polytechnic School, Copenhagen, and the coast at Elsinore.[2] In November and December of 1841, five analyses of air in Copenhagen were made, giving 20.82, 20.83, 20.78, 20.81, and 20.84 per cent of oxygen, respectively, with an average of 20.816 per cent. The author points out that these results agreed perfectly with those obtained by Dumas and Boussingault in their analyses of the air collected in Paris and on the Faulhorn, as well as with those obtained by Stas in Brussels, Marignac in Geneva, Brunner in Berne, and Verver in Gröningen.

[1] Verver, Bulletin des Sciences Physiques et Naturelles en Néerlande, 1840, p. 191.
[2] Lewy, Annales de Chimie et de Physique, 1843, ser. 3, 8, p. 425.

During August 1841, on a journey from Paris to Copenhagen, he collected samples on the North Sea, the results being 20.46, 20.42, 20.45, and 20.43 per cent, with an average of 20.44 per cent. His low values may possibly be ascribed to an error in weighing the glass balloon used. Analyses were also made of air taken at Elsinore on the coast. Three samples taken on February 18, 1842, gave 20.84, 20.83, and 20.84 per cent respectively. The average was 20.837 per cent. On the return journey from Copenhagen to France, 5 samples of air taken on the sea were collected, the percentages of oxygen being 20.88, 20.91, 20.89, 21.01, and 20.84, with an average of 20.907.

Lewy also reports analyses of samples taken at Guadeloupe and analyzed in Paris. The results show abnormally high carbon-dioxide values and low oxygen contents. When computed on the basis of carbon-dioxide-free air, the oxygen content in 9 samples varies from 20.51 to 20.93 per cent. The author is inclined to attribute the exceptionally high carbon-dioxide content to the nearby volcanoes.

In Geneva, Marignac[1] found on three different days, in January and February 1842, 20.81, 20.80, and 20.77 per cent of oxygen, with an average of 20.799 per cent. Meanwhile, Stas[2] in Brussels found in 12 different experiments during 1842 a minimum of 20.84 per cent and a maximum of 20.87 per cent, but the author points out two analyses with no error that could be accounted for in which the results showed 20.90 and 20.93 per cent. In general, however, Marignac, Lewy, and Stas, all using the method of Dumas and Boussingault, obtained results that agreed with those obtained by the latter investigators.

In studying respiration, Marchand[3] reported air-analyses made in Halle at 10 different times. The method was similar to that of Dumas and Boussingault. The percentages of oxygen obtained were as follows:

	per cent.		per cent.
1	20.99	6	20.89
2	20.97	7	20.98
3	20.98	8	20.99
4	20.90	9	21.02
5	20.96	10	21.03

The average of these values, 20.97 per cent, was employed by him as indicating the composition of normal air.

Two years later, Marchand[4] published two analyses of outdoor air in Halle which were made by the hydrogen-explosion method with results as follows: 8 a.m., 20.920 per cent; 8 p.m., 20.912 per cent.

In the attempt to establish some relationship between the composition of the air and the invasion of cholera, at least two investigations on the oxygen content of the atmospheric air during a cholera

[1] Marignac, reported by Dumas in Comptes rendus, 1842, **14**, p. 380.
[2] Stas, Comptes rendus, 1842, **14**, p. 570.
[3] Marchand, Journal für praktische Chemie, 1848, **44**, p. 1.
[4] Marchand, Journal für praktische Chemie, 1850, **49**, p. 449.

epidemic are reported in the literature,[1] *i.e.*, those of Baumgartner[2] and Laskowsky.[3]

Employing Brunner's method, Laskowsky in Moscow made a number of analyses of air during the cholera epidemic. The results, which are given in table 11, show a variation of 0.16 per cent of oxygen, which the author maintains is not far from the results of Dumas and Boussingault, who report variations of 0.19 per cent. He concludes that the air in Moscow during the time of the cholera was normal.

TABLE 11.—*Air-analyses made by Laskowsky in Moscow during the cholera in 1847.*

Date.	Time.	Oxygen.	Date.	Time.	Oxygen.
1847		*p. ct.*	1847.		*p. ct.*
Nov. 3......	Noon	20.88	Nov. 9......	Evening ..	20.77
Nov. 3......	Evening ..	20.76	Nov. 10......	Noon	20.80
Nov. 4......	Noon	20.73	Nov. 10......	Evening ..	20.87
Nov. 4......	Evening ..	20.85	Nov. 11......	Noon	20.82
Nov. 7......	Noon	20.89	Nov. 11......	Evening ..	20.77
Nov. 7......	Evening ..	20.82			
Nov. 8......	Noon	20.82	Maximum.	....	20.89
Nov. 8......	Evening ..	20.76	Minimum .	....	20.73
Nov. 9......	Noon	20.88	Average ..	....	20.82

Adding oxide of manganese to the reduced copper of the Dumas and Boussingault method to increase its absorbing action, Deville and Grandeau[4] determined the oxygen in a number of samples of air for May and June of 1859, and found as an average 20.88 per cent.

An ingenious use of an ammoniacal solution of copper chloride as an absorbent for oxygen was made by Doyere[5] in connection with studies on respiration. As the result of several analyses by this and other methods, Doyere reports that the percentage of oxygen in air is about 20.5 to 20.7, but the research does not inspire confidence.

Employing an exceptionally accurate hydrogen eudiometer designed primarily for use in their classical respiration experiments, Regnault and Reiset reported in a preliminary communication in 1848[6] a large number of analyses that were made during the three preceding years, 1845, 1846, and 1847, in Paris, as well as near Dieppe. All of these analyses showed an oxygen content between 20.85 and 20.97 per cent. In the report of their experiments on the respiration of animals,[7] the authors give a com-

[1] The early observations of Davidson, who found 67 per cent of vital air in Martinique during an epidemic of yellow fever, are only of historic interest. (Cited by Russell, Transactions of the Sanitary Institute, 1893, **13**, p. 232.)

[2] Baumgartner, loc. cit.

[3] Laskowsky, Liebig's Annalen der Chemie und Pharmacie, 1850, **75**, p. 176.

[4] Deville and Grandeau, Comptes rendus, 1859, **48**, p. 1103.

[5] Doyere, Annales de Chimie et de Physique, 1850, 3d ser., **28**, p. 5. Among the innumerable observations on the composition of the air made by Scheele, it is interesting to note that he found that one-third of the air was absorbed by an ammoniacal solution of copper. (See Scheele, Efterlemnade bref och anteckningar. Edited by A. E. Nordenskiöld, Stockholm, 1892, p. 58.)

[6] Regnault and Reiset, Comptes rendus, 1848, **26**, p. 6.

[7] Regnault and Reiset, Annales de Chimie et de Physique, 1848, 3d ser., **26**, p. 299.

plete description of their eudiometer, and report 6 air-analyses made from one sample of carbon-dioxide-free air, in order to show the accuracy of the apparatus. The results obtained were 20.936, 20.940, 20.932, 20.960, 20.946, and 20.941 per cent of oxygen, the variation being 0.028 per cent.

TABLE 12.—*Regnault's analyses of air collected in Paris.*

Date.	Place.	Oxygen.	Date.	Place.	Oxygen.
		p. ct.			*p. ct.*
1847. Dec. 24	Balcony, College of France	20.987	1848. Jan. 4	Observatory, College of France	20.929
Dec. 24	....Do	20.952 20.957	Jan. 6	....Do	20.948
			Jan. 7	....Do	20.943
Dec. 24	....Do	20.999	Jan. 8	....Do	20.956
Dec. 28	Top of Panthéon	20.962	Jan. 8	Choisy-le-Roi	20.948
	Top of Panthéon (snow)	20.963	Jan. 9	Observatory, College of France	20.981
Dec. 28	Observatory, College of France	20.956 20.939	Jan. 10	....Do	20.948
			Jan. 11	....Do	20.957
Dec. 29	Place de la Concorde	20.953	Jan. 12	....Do	20.963
Dec. 29	Observatory, College of France	20.948	Jan. 12	Choisy-le-Roi	20.947
Dec. 30	....Do	20.939 20.930	Jan. 13	Observatory, College of France	20.970 20.968
Dec. 30	....Do	20.984 20.967	Jan. 14	....Do	20.952
			Jan. 14	Panthéon	20.953
Dec. 31	....Do	20.949	Jan. 15	Observatory, College of France	20.986
Dec. 31	Top of the Panthéon	20.959	Jan. 15	Versailles	20.936
Dec. 31	Choisy-le-Roi	20.966	Jan. 15	....Do	20.922
Dec. 31	Esplanade de Vincennes	20.945	Jan. 15	....Do	20.948
Dec. 31	....Do	20.947	Jan. 15	....Do	20.954
Dec. 31	Over a cornfield	20.980 20.992	Jan. 15	....Do	20.992 20.993
1848. Jan. 1	Court, College of France	20.913	Jan. 15	....Do	20.998
Jan. 3	Observatory, College of France	20.934	Jan. 15	....Do	20.952

It is to Regnault that we are indebted for the first extensive international investigation on the composition of the air. This carefully planned coöperative investigation was in part disturbed by the political differences in Europe during 1848, but in spite of the difficulties encountered, Regnault finally succeeded in getting together a large number of samples, which he analyzed.[1] Air was collected in Paris and other parts of France, in Berlin, Madrid, Switzerland, on the Mediterranean Sea, on the Atlantic Ocean, in Ecuador, on the coast of Africa, in India, and on the Pacific and Arctic Oceans, thus representing by far the most extensive investigation on the composition of atmospheric air that has ever been undertaken. Indeed, it may be stated that no subsequent investigation has approached it in completeness with regard to the geographical collection of samples. Regnault made arrangements to have these sam-

[1] Regnault, Annales de Chimie et de Physique, 1852, 3d ser., **36**, p. 385.

ples collected on the 1st and 15th of each month at about the hour of true midday in each place. The samples were then sent to Paris, where they were analyzed by explosion with hydrogen in the apparatus used for analyzing the samples of Paris air.

About 100 analyses were made of air collected in Paris or its suburbs, the larger number being taken at the observatory of the College of France. A part of the results are given in table 12, showing the variations on the different days and the accuracy of the analyses made on the same sample as indicated by the close agreement of the duplicate determinations.

The smallest amount of oxygen found was 20.913 per cent, the largest 20.999 per cent, and the general average, 20.96 per cent. The extreme difference, 0.086 per cent, is greater than the errors resulting from the experiments themselves, for this rarely exceeds 0.02 per cent. Regnault concludes that the absolute change is so small that one can easily attribute this to local alterations which would be frequently found in the center of large cities. He notes further that the variations found at different hours of the same day are no smaller than the variations between days.

The results of the analyses of air collected at other points in France are given in table 13.

TABLE 13.—*Regnault's analyses of air collected in France outside of Paris.*

Montpellier.		Lyon.		St. Martin-aux-Arbres, Normandy.	
Date.	Oxygen.	Date.	Oxygen.	Date.	Oxygen.
1848.	*p. ct.*	1848.	*p. ct.*	1848.	*p. ct.*
Feb. 1....	{ 20.929 20.948	Feb. 1....	20.966	Feb. 29	20.952
Feb. 15....	20.962	Feb. 15....	20.930		
Mar. 15....	{ 20.959 20.968	Mar. 15....	20.918		
Apr. 1....	20.940				
Apr. 15....	20.952				

TABLE 14.—*Regnault's analyses of air collected in Berlin.*

Date.	Oxygen.	Date.	Oxygen.	Date.	Oxygen.
1848.	*p. ct.*	1848.	*p. ct.*	1849.	*p. ct.*
Feb. 1....	20.967	Aug. 16....	20.910	Feb. 15....	20.993
Feb. 15....	20.959	Sept. 15....	20.943	Mar. 15....	20.980
Mar. 15....	20.956	Oct. 1....	20.976	Apr. 1....	20.962
Apr. 1....	20.958	Oct. 15....	20.986	Apr. 16....	20.947
Apr. 15....	20.963	Nov. 2....	20.936	May 3....	20.976
May 1....	{ 20.941 20.953	Nov. 15.... Dec. 1....	20.946 20.996	May 17.... June 3....	20.967 20.967
May 15....	20.937	Dec. 15....	20.919	June 15....	20.966
June 15....	{ 20.943 20.933	1849. Jan. 1....	 20.981	July 1....	20.998
July 1....	20.908	Jan. 15....	20.962		
July 15....	20.903	Feb. 3....	20.973		

Samples were also collected at noon in Berlin by Magnus from February 1, 1848, to July 1, 1849; at the Madrid Observatory in 1848; and at

different places in Switzerland; the results are reported in tables 14, 15, and 16, respectively.

TABLE 15.—*Regnault's analyses of air collected at Madrid.*

Date.	Oxygen.	Date.	Oxygen.
1848.	p. ct.	1848.	p. ct.
Feb. 15....	20.922	Aug. 15....	20.963
Mar. 1....	20.953	Sept. 1....	20.982
May 15....	20.973		20.964
June 15....	20.916	Sept. 15....	20.975
July 15....	20.924	Oct. 1....	20.970
Aug. 1....	20.974		

TABLE 16.—*Regnault's analyses of air collected in Switzerland.*

Date.	Place.	Oxygen.	Date.	Place.	Oxygen.
1848.		p. ct.	1848.		p. ct.
Jan. 15	Mont Salève.....	20.940	Sept. 1	Obs. of Geneva......	20.924
		20.953	Sept. 6	Montanvert (valley of Chamounix)...	20.963
Feb. 1	Obs. of Geneva...	20.946			
		20.935	Sept. 8	Mont Buet (Savoy).	20.930
Feb. 1	Mont Salève.....	20.963	Oct. 1	....Do.............	20.981
		20.957	Nov. 1	Obs. of Geneva.....	20.969
Apr. 1	Obs. of Geneva.....	20.920	Nov. 15	....Do.............	20.990
Apr. 1	Mont Salève.......	20.928	Dec. 1	....Do.............	20.955
June 15	Obs. of Geneva.....	20.956	Dec. 15	....Do.............	20.913
July 1	....Do............	20.903	1849.		
July 15	....Do............	20.935	Jan. 15	....Do.............	20.959
Aug. 1	....Do............	20 937	Feb. 1	....Do.............	20.993
Aug. 15	....Do............	20.961	Feb. 15	....Do.............	20.982

The percentage of oxygen in these different samples of air collected in various parts of Europe ranged from 20.903 to 21, that is to say, it had approximately the same limit of variation as the air collected in Paris.

Regnault fortunately secured the cooperation of a number of travelers, and hence was able to extend his observations considerably. The results are given in tables 17 to 20.

TABLE 17.—*Analyses of air collected on the Mediterranean Sea.*

Date.	Place.	Oxygen.	Date.	Place.	Oxygen.
1851.		p. ct.	1851.		p. ct.
May 4	At sea, SE.of Minorca, lat. 38° 18′ N.; long. 1°16′ E.....	20.970	May 28	Toulon harbor.....	20.935
			June 8	At sea, 70 miles NNE. of Algiers.	20.961
May 20	Toulon harbor	20.912	June 5	Algiers.........	20.420
May 21	....Do............	20.931			20.395
May 22	....Do............	20.951	June 9	At sea, S. of Minorca, lat. 39°0′ N.; long. 1°32′ E....	20,927
May 22	....Do............	20.970			
May 24	....Do............	20.950			
May 25	....Do............	20.960	June 27	Toulon harbor	20.982
May 27	....Do............	20.854	June 28	....Do..........	20.928
		20.872	June 29	....Do..........	20.955
May 27	....Do............	20.979	June 30	....Do.....	20.964

TABLE 18.—*Analyses of air collected on the Atlantic Ocean, between Liverpool and Vera Cruz.*

Date.	Place.	Oxygen.
1848.		*p. ct.*
Apr. 1	At sea, lat. 34° 21′; long. 24° 40′	{ 20.922 20.920
Apr. 26	Near St. Domingo, lat. 20°; long. 72° 30′	{ 20.920 20.918
May 11	Vera Cruz	20.962
May 2	Entrance to Gulf of Mexico, lat. 21° 50′; long. 88° 40′	20.953
May 7	Bay of Vera Cruz	20.965

TABLE 19.—*Analyses of air collected at different parts of the East Indian Ocean.*

Date.	Place.	Oxygen.
1848.		*p. ct.*
July 5	Bay of Goree (Senegal)	20.896
Sept. 15	Lat. 33° 40′ S.; long. 16° 15′ E.	{ 20.843 20.854
1849.		
Jan. 15	Long. 78° 38′ E.; lat. 2° 29′ S.	20.975
Feb. 1	Gulf of Bengal; lat. 9° 4′ N.; long. 83° E.[1]	{ 20.460 20.453
Mar. 8	On the Ganges, near Calcutta, noon.[2]	{ 20.390 20.387
Mar. 15	Calcutta	20.866
Mar. 24	On the Hoogly River (East Indies), opposite Kedgerre, lat. 21° 53′ N.	{ 20.920 20.921 20.928
Aug. 25	Mayotte, off Mozambique	20.910
Dec. 15	Simons Bay (Cape of Good Hope)	20.936
1850.		
Mar. 19	Mers-el-Kébir (coast of Africa)	20.870

[1] The air contained 0.057 per cent of carbon dioxide.

[2] A note in connection with this sample says on March 8 there was a sudden invasion of cholera and no samples were taken until March 15. The weather was excessively foggy during the night, and the fogs did not disappear during the day; the air was full of putrefying vegetable and organic matter, and there were many dead bodies in the river. The air contained 0.133 per cent of carbon dioxide.

Two exceptions to the usual results appear in samples of air taken in Toulon Harbor on May 27 at 8^h 30^m a. m., duplicate analyses giving 20.854 and 20.872 per cent of oxygen, respectively. These numbers are appreciably less than the minimum which was obtained in the air of Paris, but the air collected on June 5 at 11 p. m. in the port of Algiers gave even lower results, these being 20.420 and 20.395 per cent, respectively. The author does not question the sealing of the tubes, as it was done by a person who had had experience in his own laboratory.

In Ecuador two samples were taken; one which was collected in the village of Guallabamba on August 3, 1848, at 8^h 15^m in the morning gave 20.960 per cent; the other, taken on the summit of Pichincha—a mountain higher than Mont Blanc—on May 15, 1849, at 12^h 45^m p. m., gave 20.949 and 20.988 per cent, respectively.

Among the analyses of air collected on the East Indian Ocean (see table 19), only two show a composition very different from that of normal

air. The analysis of air collected on February 1, 1849, in the Gulf of Bengal, gave 20.460 and 20.453 per cent of oxygen. The notes which accompany this sample do not present anything of distinct interest. The air collected on the Ganges on March 8, 1849, shows 20.390 and 20.387 per cent of oxygen, and Regnault maintains that the conditions set forth in the notes accompanying this sample explain this anomalous case. Four other samples taken in 1852 at different points in the Pacific and South Atlantic Ocean gave 21.015, 20.935, 20.950, and 20.963 per cent of oxygen, respectively. Samples of air from the Arctic Ocean were also analyzed, these being given in table 20.

TABLE 20.—*Analyses of air collected on the Arctic Ocean.*

Date.	Place.	North latitude.		East longitude.		Oxygen.
1848.		°	′	°	′	*p. ct.*
June 1	Cape Farewell	60	10	39	14	20.91
June 20	Whale Island	67	5	55	9	20.91
July 1	Black Hook	70	20	55	30	20.92
Oct. 15	Port Leopold	73	52	90	12	20.93
Oct. 15	....Do	73	52	90	12	20.93
Nov. 15	....Do	73	52	90	12	20.85
1849.						
Jan. 15	Port Leopold	73	52	90	12	20.91
Mar. 1	....Do	73	52	90	12	20.89
Mar. 15	....Do	73	52	90	12	20.86
Mar. 15	....Do	73	52	90	12	20.86
Apr. 15	....Do	73	52	90	12	20.90
Apr. 15	....Do	73	52	90	12	20.94
May 1	....Do	73	52	90	12	20.93
May 1	....Do	73	52	90	12	20.91
Aug. 1	....Do	73	52	90	12	20.87
Aug. 15	....Do	73	52	90	12	20.94
Aug. 15	....Do	73	52	90	12	20.94

Regnault's conclusions are: (1) that the air of our atmosphere usually presents variations in composition which are sensible but very small, for the percentage of oxygen varies generally only from 20.9 to 21.0, although in certain cases, apparently more frequent in the warm countries, the proportion of oxygen may fall to 20.3 per cent; (2) that the average percentage of oxygen contained in the air of Paris during the year 1848 was 20.96.

The importance of a geographical study of the composition of the atmosphere was so keenly felt that the French Academy commissioned Lewy[1] to make analyses of air while on a voyage to South America. The analyses were made by the method of Regnault and Reiset. Previous to taking this journey, he made several analyses of air in France. On September 6, 1847, Lewy found as a result of three analyses of air in Paris, 21.018, 21.015, and 21.008 per cent, with an average of 21.014 per cent. In Havre, he found on November 22, 1847, that in three analyses the percentages of oxygen were 20.895, 20.880, and 20.888, with an average of 20.888 per cent.

[1] Lewy, Annales de Chimie et de Physique, ser. 3, 1852, **34**, p. 5.

The analyses of the atmospheric air collected on the Atlantic Ocean and the Caribbean Sea are reported in table 21, the results giving an average of 0.046 per cent for carbon dioxide and 21.03 per cent for oxygen. On examining his figures, Lewy found that the composition of the air collected during the day differed from that collected during the night, the air of the day being richer in carbon dioxide and oxygen. He accordingly averaged his results for both the day and the night, obtaining the following values: for the day, carbon dioxide 0.053 per cent, oxygen 21.06 per cent; for the night, carbon dioxide 0.0346 per cent, oxygen 20.97 per cent.

TABLE 21.—*Analyses of air collected on the Atlantic Ocean and the Caribbean Sea.*

Date.	Latitude N.		Longitude W. from Paris.		Average of 3 analyses of each sample.	
					Carbon dioxide.	Oxygen.
1847.	°	′	°	′	*p. ct.*	*p. ct.*
Dec. 1	47	30	10	5	0.0488	21.05
Dec. 4	47	00	13	0	.0334	20.96
Dec. 8	35	40	20	35	.0550	21.06
Dec. 17	22	5	39	0	.0577	21.06
Dec. 18	21	45	41	3	.0335	20.96
Dec. 18	21	9	42	25	.0542	21.06
Dec. 19	20	35	43	35	.0339	20.96
Dec. 26	15	49	64	28	.0529	21.06
Dec. 28	14	6	70	4	.0509	21.06
Dec. 30	12	5	76	0	.0514	21.06
Dec. 31	......		......		.0377	21.01

Lewy concludes that the difference between the oxygen and carbon dioxide in the atmospheric air on the ocean and in normal air becomes more noticeable the farther away one goes from the land. He further says that it is impossible to attribute this difference to errors in analysis, as he maintains that two analyses of air do not differ by more than 1 part in 10,000. According to his interpretation of the results, this difference is caused by the fact that the water of the ocean gives off carbon dioxide and oxygen. During the day the surface of the sea becomes warmed by the sun's rays and a part of these gases is dissolved; during the night, on the contrary, this influence is not felt.

Results of analyses of air samples collected in New Granada on a trip from Santa Marta to Montserrat are given in table 22, while the results obtained from air collected in 1850 in Bogota, at a height of 2645 meters, with an average barometer of 565 mm., are reported in table 23. The high values for carbon dioxide are attributed to the presence of volcanoes 3 or 4 hours distant from Bogota.

In a general résumé of the subject, the author concludes that by examining these results (tables 21 to 23), one sees that the composition of the air up to a height of about 3000 meters is nearly the same in the New

World as in the Old World, but not absolutely constant. The increase in the percentage of carbon dioxide, which rose as high as 0.49 per cent—14 or 16 times the normal percentage—is attributed by Lewy to the influence of large forest fires and the presence of volcanoes.

TABLE 22.—*Analyses of air from New Granada.*

Date.	Place.	Elevation.	Average of 3 analyses of each sample.	
			Carbon dioxide.	Oxygen.
1848.		*meters.*	*p. ct.*	*p. ct.*
Jan. 25	Santa Marta	0	0.046	21.02
Feb. 7	Mompox	38	.031	21.05
Feb. 18	Magdalena River	..	.033	21.03
Mar. 3	....Do	..	.046	21.00
Mar. 29	Honda	242	.032	20.99
Aug. 5	Ambalema	282	.112	20.55
Aug. 2	Esperanza...............	396	.245	20.33
Apr. 2	Guaduas	996	.031	21.00
Aug. 2	Santa Ana..............	998	.123	20.54
July 8	Bogota	2645	.050	21.03
July 8	Montserrat	3193	.052	20.99

TABLE 23.—*Analyses of air from Bogota (2645 meters).*

Date.	Carbon dioxide.	Oxygen.	Date.	Carbon dioxide.	Oxygen.
1850.	*p. ct.*	*p. ct.*	1850.	*p. ct.*	*p. ct.*
Mar. 7	0.0386	21.02	Sept. 2	0.1704	21.03
Apr. 12	.0366	21.00	Sept. 3	.1585	21.02
May 8	.0361	20.99	Sept. 3	.4896	21.03
May 9	.0382	20.99	Sept. 3	.4904	21.03
June 15	.0419	21.00	Sept. 4	.1326	21.03
July 24	.0425	21.02	Sept. 4	.0865	21.00
Aug. 19	.0504	21.01	Sept. 8	.1283	21.02
Aug. 23	.0481	21.02	Sept. 9	.0751	21.03
Sept. 1	.0618	21.02	Sept. 10	.0458	21.03
Sept. 2	.0765	21.02	Sept. 12	.0471	21.03
Sept. 2	.1629	20.97	Oct. 3	.0475	21.02

The hydrogen-explosion method and the weighing of the amount of oxygen absorbed by a metal or by phosphorus involved an exceedingly elaborate technique and restricted the number of observations that could possibly be made by one man in a day. In 1851 there appeared the description of a method of absorbing oxygen by means of an alkaline solution of pyrogallic acid. Liebig[1] reported the results of 11 analyses, with percentage values as follows: 20.99, 20.89, 21.03, 20.95, 20.77, 20.92, 20.90, 20.80, 20.75, 20.76, 20.93. With this method he maintained that in an hour half a dozen analyses could be carried out. Gallic acid could also be used instead of pyrogallic acid, although, according to Liebig, the absorption required a longer time than with pyrogallic acid, *i.e.*, 1½ to 2 hours instead of as many minutes. Liebig gives the results of 8 analyses

[1] Liebig, Annalen der Chemie und Pharmacie, 1851, 77–78, p. 107.

obtained with gallic acid with percentages of oxygen as follows: 20.59, 20.69, 20.97, 20.52, 21.35, 20.80, 20.78, and 21.19.

This method was destined to become one of the most important methods for technical gas-analysis that had ever been devised. It is interesting to note that at this date (1912) practically all of the exact gas-analysis apparatus employ the alkaline solution of pyrogallol. Almost immediately after the introduction of the method it was found that under certain conditions the interaction of air with pyrogallic acid and potassium hydroxide resulted in the formation of slight quantities of carbon monoxide. This for a time discouraged observers from using the method. Subsequently conditions were so adjusted as to minimize this apparent error.

Using a modification of the Regnault method, Frankland and Ward[1] published 6 analyses of air as an indication of the accuracy of the apparatus. The results given are 20.880, 20.888, 20.883, 20.867, 20.868, and 20.876 per cent, with an average of 20.877 per cent, the greatest difference being only 0.021 per cent.

Frankland in 1861,[2] reporting the results of some air samples taken by himself on an excursion to the top of Mont Blanc, cites analyses of air collected during a balloon ascension in August 1852, which were made by Dr. Miller. At a height of 18,000 feet the oxygen percentage was found to be 20.88; a sample taken at the same time at the surface of the earth gave 20.92 per cent.[3]

Frankland's analyses of the air from Mont Blanc were made by absorbing the carbon dioxide by means of caustic potash, and determining the oxygen by explosion with electrolytically prepared hydrogen. Specimens were taken at Chamounix (altitude 3000 feet), at the Grands Mulets (11,000 feet), and at the top of Mont Blanc (15,732 feet). At Chamounix the percentages of oxygen found were 20.892 and 20.870, and of carbon dioxide, 0.063. At the Grands Mulets, two samples showed 20.793 and 20.765 per cent of oxygen and 0.111 per cent of carbon dioxide. At the summit of Mont Blanc, on August 21, at 8^h 45^m a.m., two samples gave 20.950 and 20.951 per cent of oxygen respectively, and 0.061 per cent of carbon dioxide. The averages of all the results are, therefore, as follows:

Place.	Carbon dioxide.	Oxygen.
	p. ct.	*p. ct.*
Chamounix	0.063	20.894
Grands Mulets	.111	20.802
Summit of Mont Blanc	.061	20.963

[1] Frankland and Ward, Quarterly Journal of the Chemical Society, London, 1854, **6**, p. 197.

[2] Frankland, Quarterly Journal of the Chemical Society, London, 1861, **13**, p. 22.

[3] Julius Hann in his Lehrbuch der Meteorologie, Leipzig, 1901, p. 9, states that samples of air were collected in a balloon journey made by Welsh; according to the analyses made by Miller, the oxygen content on the surface of the earth was found to be 20.92 per cent; at 4100 meters, 20.89; at 5500 meters, 20.75; and at 56.80 meters, 20.89 per cent.

Two series of analyses of the air of Madrid were made by Torres Muñoz.[1] The percentages of oxygen are very small, and those of carbon dioxide usually very high, the latter ranging from 0.02 to 0.09 per cent. The oxygen was determined in part by cuprous ammonium chloride and in part by potassium pyrogallate. The percentages of oxygen obtained are given in table 24.

TABLE 24.—*Analyses of air collected in Madrid by Torres Muñoz.*

Oxygen outside the walls, in March.		Oxygen within the walls, in April.	
p. ct.	*p. ct.*	*p. ct.*	*p. ct.*
20.71	20.70	20.70	20.78
20.79	20.74	20.70	20.69
20.77	20.69	20.77	20.70
20.77	20.81	20.75	20.78
20.73	20.79	20.70	20.80
20.75	20.78	20.69	20.73

Another investigator, Russell,[2] using a modified Bunsen apparatus, reports in 1868 an analysis of air as containing 20.845 per cent of oxygen.

One of the first to use the pyrogallic-acid method for the analysis of atmospheric air was Schiel,[3] who in 1857 determined the oxygen content of air at an altitude of 2330 feet on the boundary between Kansas and Colorado, finding 20.91 per cent as an average of three experiments.

The importance of Liebig's discovery of the use of potassium pyrogallate as an absorbing agent for oxygen was early recognized by Speck,[4] who submitted the method to numerous tests in connection with his physiological researches. Speck recommends the use of barium hydroxide in place of potassium hydroxide to prevent the formation of carbon monoxide. The analyses with barium hydroxide and pyrogallic acid agreed well with the Bunsen explosion method. Duplicate analyses by the barium pyrogallate method gave results as follows:

Date.	I.	II.
1866.	*p. ct.*	*p. ct.*
Sept. 23	20.98	20.97
Oct. 10	20.93	20.96
Oct. 11	20.93	20.98

One of the most extensive investigations of the oxygen content of atmospheric air was that carried out by R. Angus Smith, of Manchester,

[1] Estudios quimicos sobre el aire atmosférico de Madrid, por D. Ramon Torres Muñoz de Luna, Madrid, 1860. A translation of this entire paper was made by de Chambry and published in Annales d'Hygiene Publique et de Médicine légale, 1865, series 2, **15**, p. 337.

[2] Russell, Journ. Chem. Soc., London, 1868, new ser., **6**, p. 140.

[3] Schiel, Annalen der Chemie und Pharmacie, 1857, **103**, p. 120.

[4] Speck, Schriften der Gesellschaft zur Beförderung der gesammte Naturwissenschaft zu Marburg, 1871, **10**.

England. His results, which were first published in a condensed form,[1] were subsequently given more in detail as a part of a larger publication.[2] Using for the most part the explosion apparatus of Bunsen, although making several ineffective attempts to secure accurate results by means of Liebig's pyrogallic-acid method, Smith made an enormous number of analyses of outdoor air in connection with his investigation of the ventilation of houses. In his book, which contains the best collection of the literature and analyses of outdoor air thus far published in English, he reports over 100 determinations of the oxygen content of outdoor air. Firmly impressed with the belief that the presence of putrefying organic matter requires a material draft upon the oxygen of the air, Smith made a comparative study of the air collected at the front door of the laboratory and in outhouses in the near neighborhood. His results are given in table 25.

TABLE 25.—*Determinations made by Smith of oxygen in outdoor air and in the air of outhouses in Manchester.*

Date.	Air from front door of laboratory.	Air from outhouses.	Date.	Air from front door of laboratory.	Air from outhouses.
1863.	*p. ct.*	*p. ct.*	1863.	*p. ct.*	*p. ct.*
Dec. 1	20.90	20.80	Dec. 19	20.87	....
Dec. 10	20.96	20.85	Dec. 21	20.92	20.56
Dec. 11	20.98	20.79	Dec. 21	21.02	20.79
Dec. 11	20.90	20.72	Dec. 21	20.88	20.64
Dec. 15	20.90	20.87	Dec. 21	20.91	20.94
Dec. 15	20.02	20.76	Dec. 21	21.01	20.67
Dec. 17	20.96	20.59	Dec. 22	20.96	20.53
Dec. 17	20.78	20.85	Dec. 22	20.92	20.71
Dec. 17	20.83	20.90	1864.		
Dec. 18	20.91	20.21	Feb. 26	21.01	20.66
Dec. 18	20.92	20.58	Feb. 24	21.05	....
Dec. 18	20.87	20.74	Feb. 20	20.98	....
Dec. 18	21.02	20.40	Feb. 20	20.99	....
Dec. 18	21.00	20.77	Feb. 20	21.01	....
Dec. 19	20.83	20.99	Feb. 20	20.94	....
Dec. 19	20.98	20.70			
Dec. 19	20.88	20.82	Average	20.943	20.70
Dec. 19	21.01	20.46			

A very extensive examination of the air of London was carried out by Smith in November 1869. These analyses give us a method of judging of the accuracy of Smith's method and the agreement of duplicates. They are in part reported in table 26.

The probable influence of weather conditions, especially moisture and fog, led Smith to investigate the changes in oxygen content as affected by this factor. Five analyses are reported of air taken near the laboratory in Manchester during wet weather, the results being 20.90, 21.01, 21.01, 21.05, and 20.96 per cent of oxygen, respectively, with an average

[1] Smith, Memoirs of the Literary and Philosophical Society of Manchester, 1864–65, ser. 3, 3, p. 5.
[2] Smith, Air and rain; the beginnings of a chemical climatology. London, 1872.

of 20.98 per cent. In dry and foggy weather, when the smoke of Manchester hung over the town, the results were as follows:

	Oxygen percentage.
Near center of town	20.90 20.88
At laboratory	20.90 20.96
At laboratory, afternoon	20.91
At laboratory, forenoon	21.01
At laboratory, afternoon	20.82
Average	20.91

TABLE 26.—*Determinations made by Smith of oxygen in London air.*

Place.	First analysis.	Second analysis.	Average.
	p. ct.	*p. ct.*	*p. ct.*
Islington, Duncan Terrace	20.86	20.81	20.835
Hoxton, Hoxton Square	20.85	20.82	20.835
Dalston, Albion Road	20.90	20.91	20.905
Hackney, near Hackney Station	20.82	20.85	20.835
Clarendon Square, Somers Town	20.90	20.89	20.895
Alpha Road and Grove Road	20.87	20.80	20.835
Average	.....	.....	20.857
Parks and open places.			
Near Belsize Park	21.02	21.00	21.010
Kennington Park	20.96	20.92	20.940
Chelsea Hospital, gardens near river	20.91	20.91	20.910
Vauxhall Bridge, near river	20.90	20.91	20.905
Houses of Parliament, terrace	20.96	20.93	20.945
Hyde Park, Sloane Street	20.91	20.94	20.925
Middle of Hyde Park	21.03	20.98	21.005
Average	.....	.....	20.95

In a very dense fog, which Smith states was a rare experience in Manchester, and which made the eyes smart and walking difficult, he found 20.82 and 20.89 per cent of oxygen. In the yard back of the laboratory he regularly found somewhat less oxygen than in the front, his results being 20.80, 21.01, 20.94, 20.84, 21.09 per cent, respectively, with an average of 20.936 per cent. He summarized his results as follows:

	Oxygen percentage.
In very wet weather, in front of the laboratory	20.98
At all times (average of 32 experiments)	20.947
Behind the laboratory, in medium weather	20.936
In foggy frost	20.91
In outhouses	20.706

If we except the air from outhouses, we find an average variation in these analyses of 0.07 per cent.

During 1863 to 1865 Smith made an extensive examination of the air at both the summit and base of a number of mountains in Scotland. While the altitudes were by no means as great as those of the Alps, and hence the results, which are given in table 27, can not contribute exten-

sively to the question of the Dalton hypothesis, nevertheless they are extremely interesting as showing careful attention to a very important problem.

TABLE 27.—*Determinations made by Smith of oxygen in the air from mountainous districts of Scotland.*

Place.	Summit.	Base.	Place.	Summit.	Base.
	p. ct.	p. ct.		p. ct.	p. ct.
Ben Nevis	20.91	20.93	Ben Lomond	21.08	....
Do	20.96	20.91	Do	20.91	....
Do	20.94	20.89	Ben Muich Dhu	21.00	....
Do	20.88	....	Do	21.07	....
Do	21.01	....	Do	21.02	....
Lochin-y-gair (Balmoral)	20.94	20.80	Do	20.99	....
Do	20.95	21	Do	20.93	....
Ben Ledi	20.98	21.02	Do	21.01	....
Do	20.97	....	Ochill Hill	21.05	....
Do	20.97	....	Do	21.07	....
Ben Voirlich	21.01	20.87	Moncrieffe Hill	20.93	....
Do	....	20.88			
Ben-na-bourd	21.03	21.18	Average	20.98	20.94
Ben Lomond	20.94	20.95			

For comparison, Smith analyzed a large number of samples of air from districts in Scotland with but slight, if any, elevation. (See table 28.) Of particular significance is the extremely low value found near Inverness, which Smith attributes to some impurity arising from the water.

TABLE 28.—*Determinations made by Smith of oxygen in air from districts not mountainous.*

Place.	Oxygen.	Average.	Place.	Oxygen.	Average.
	p. ct.	p. ct.		p. ct.	p. ct.
Shore at Lossiemouth	21.05	....	Errol, marshy ground[3]	20.91	....
Do	20.95	21.00	Do.	20.96	20.94
Inverness, at Moray Frith	20.89	....	Caledonian Canal (near Inverness)[4]	20.88	....
Do	20.89	....	Balmoral	20.88	....
Do	20.86	20.88	Do	21.00	20.90
Inverness, behind the town[1]	20.88	....	Taynuilt (near Oban)	20.92	....
Sea-shore, Oban	20.98	....	Do	20.86	20.89
Edinburgh, Prince's street	20.99	....	Braemar-on-the-Dee[5]	21.18	....
Do	20.92	....	Huntly	21.03	....
Edinburgh, Calton Hill	20.94	20.95	Mar Forest[6]	21.04	....
Aboyne	20.94	....	Do	21.02	....
Do	20.95	....	Do	21.08	....
Do	21.02	20.96	Do	20.88	21.00
Aberdeen, sea-shore[2]	21.05	....	Forest near Braemar	20.87	....
Do	21.01	....			
Do	21.07	21.04	Total average	....	20.96

[1] Very clear weather.
[2] Wind from sea, N.; evening.
[3] Windy and cloudy.
[4] Cloudy and windy, SW.
[5] Cloudy.
[6] Rain and sunshine.

Although unquestionably slightly affected by the carbon dioxide in the exhalations of the inhabitants and in the production of furnaces and stoves in Perth, the results of Smith's analyses of air collected from a

number of alleys and narrow streets in this city are also given here (see table 29).

TABLE 29.—*Determinations made by Smith of oxygen in air from the worst places in Perth.*[1]

Place.	Oxygen.	Place.	Oxygen.
	p. ct.		*p. ct.*
Close, 70 South street	20.87	Long Close, off George street	20.90
Close, 44 Pomarium	20.92	Close, 28 Watergate	21.02
Do	20.94	Close, 82 South street	21.01
Do	20.93	Hewat's Close, 148 South st.	20.97
Weaver's Close, Pomarium	20.96	Do	21.00
Do	20.94	Close, 44 Meal Vennel	20.90
St. Paul's Close	20.96		
Do	20.99	Average	20.95
Long Close, off George street	20.94		

[1] Results of determinations made on air which was obviously indoor have been omitted.

The results found by Smith in Scotland in 1863-5 are summarized by him as follows:

	Av. p. ct. of oxygen.
Sea-shore and heath	20.999
Summit of hills	20.98
Base of hills	20.94
Places not mountainous	20.978
Inferior parts of town (favorable, i.e., windy weather)	20.95
Lower places, marshy, etc.	20.922
Forests	20.97
Total average	20.96

During a visit to Switzerland in August 1864, Smith collected a number of samples of air and determined the oxygen. In giving the results, he includes for comparison a series of four analyses of air taken in the following month among some brushwood at Reddish, near Manchester. (See table 30.)

TABLE 30.—*Determinations made by Smith of oxygen in air from marshy or confined places, Switzerland.*

Place.	Oxygen.	Average.	Place.	Oxygen.	Average.
	p. ct.	*p. ct.*		*p. ct.*	*p. ct.*
Sion, upper valley of the Rhône, Switzerland, over water and marshy grass (morning)	20.86	....	Lauterbrunnen	20.94 20.97 20.95	20.953
Sion, over water and brushwood (morning)	21.01	....	Chamounix, Montanvert	21.03 20.99	21.01
	20.94	....	Verdin, in the Sologne	20.97 20.90	20.95
	21.05	....	Vouzerou	21.01	....
	21.02	....		20.90	....
	20.96	20.95	Reddish, near Manchester, England, among brushwood	20.92 20.98 20.95 20.90	20.937
	20.94	....			
	20.95	....			
	20.83	....			
	21.00	....			
	20.90	....			

Again, in the winter of 1869 a large number of analyses were made of air collected in both the congested portions and the open parts of the city of Glasgow. The results are given in table 31.

TABLE 31.—*Determinations made by Smith of oxygen in air from Glasgow.*

Place.	Oxygen.		
	First analysis.	Second analysis.	Average.
Congested sections.	*p. ct.*	*p. ct.*	*p. ct.*
Buchanan street, near Western Club	20.92	20.91	20.915
Exchange, front of	20.89	20.90	20.895
Union street	20.88	20.88	20.880
Miller street, Argyle street	20.90	20.93	20.915
Argyle street, near Queen street	20.96	20.90	20.930
St. Enoch's Square	20.92	20.91	20.915
Cross	20.90	20.85	20.875
Blackboy Close, Gallowgate	20.90	20.88	20.890
Gallowgate, between Kent street and barracks	20.88	20.87	20.875
A close, High street	20.87	20.86	20.865
Armour street, near barracks	20.86	20.88	20.870
Kirk street	20.88	20.87	20.875
Coulter's lane, Abercromby street	20.88	20.88	20.880
A small court, Tobago street	20.85	20.90	20.875
Oswald street, Dalmarnock road	20.87	20.89	20.880
Average	....	....	20.8890
Open sections.			
Tennant street, St. Rollox	20.90	20.93	20.915
Charles street	20.92	20.92	20.920
Middleton place	20.94	20.95	20.945
Castle street, near the cathedral	20.92	20.87	20.895
Dobbies Loan, near poorhouse	20.93	20.91	20.920
New City road, near Abercorn street	20.91	20.92	20.915
Blythswood Square	20.94	20.95	20.945
Renfrew street	20.90	20.92	20.910
Newton Terrace, Sauchiehall street	20.95	20.99	20.970
University, Gilmour Hill	20.88	20.92	20.900
Quay, near Broomielaw Bridge	20.95	20.90	20.925
Anderston quay	20.90	20.90	20.900
Sharpe's lane, Stobcross street	20.98	20.97	20.975
Finnieston quay	20.90	20.92	20.910
Pointhouse pier	20.98	21.01	20.995
Average	....	....	20.9293
Total average	....	....	20.9092

Smith also cites two analyses made of air collected by a friend in the West Indies. In one taken on the North Atlantic, latitude 43° 5′ N., longitude, 17° 12′ W., at a point 18 feet above water, at 2^h 30^m p. m. on a fine day, he found 21.01, 21, and 20.97 per cent of oxygen, respectively, the average being 20.99 per cent. In a sample taken at St. John's, Antigua, on April 11, 1865, at 9 a. m. on a showery morning, three analyses of the same sample gave 20.96, 20.91, and 21 per cent, with an average of 20.95 per cent. Smith considers the difference between these two analyses as significant, and discusses the possibility of an influence on races,

and sections of the same race, of small variations in the amount of oxygen in the atmosphere.

Finally, Smith distinguishes between pure and impure air (such as that collected in outhouses) and maintains that pure air deviates from 21 by 0.065 per cent.

Hinman,[1] using an explosion apparatus, made analyses of air freed from carbon dioxide, obtaining on April 25, 1874, 20.94 and 20.93 per cent of oxygen, and on April 26, 1874, 20.94 and 20.92 per cent of oxygen, respectively.

Using Bunsen's method, A. R. Leeds[2] analyzed many samples of air collected in July, August, and September of 1876, near Hoboken, New Jersey, at the Centennial Exposition in Philadelphia, and at several places in the Adirondack Mountains. His results are given in table 32.

Table 32.—*Determinations of oxygen made by Leeds in samples of outdoor air.*

Date.	Location.	Oxygen.	Date.	Location.	Oxygen.
1876.		*p. ct.*	1876.		*p. ct.*
July 4	Stevens Institute..	20.957	Sept. 7	Stevens Institute	20.932 20.944
Aug. 2	....Do..........	20.957			
Aug. 11	....Do..........	20.821 20.843	Aug. 15	Centennial grounds	20.962
			Aug. 18	....Do..........	20.918
Aug. 29	....Do..........	20.954	Sept. 26	Stevens Institute..	20.915
Aug. 30	....Do..........	20.934	July 17	Keene Flats, Adirondacks.......	21.029
Aug. 31	....Do..........	20.942			
Sept. 1	....Do..........	20.952 20.957	July 21	Mount Marcy (summit).	20.928 20.926

In testing a gas-analysis apparatus, using copper immersed in an ammoniacal solution of ammonium chloride to absorb oxygen, Schlösing[3] found 20.80 and 20.96 per cent oxygen in two samples.

In the decade between 1879 and 1889 an unusually large number of researches on the composition of the air appeared, each of far-reaching importance. Prominent among these are the papers of von Jolly, Morley, Kreusler, Vogler, and Hempel.

No paper since that of Regnault stimulated so much subsequent research on the composition of the air as did the publication of von Jolly's[4] investigation. Working with extreme care in an attempt to weigh the gases in atmospheric air, he found in 1876 changes in oxygen content amounting to 0.5 per cent. Placing in the bulb of an air thermometer a copper spiral which could be heated by an electric current to incandescence, von Jolly was able to absorb the oxygen by the heated copper and thus determine the percentage of oxygen. His apparatus was extremely ingenious and also very complicated. His results are given in table 33.

[1] Hinman, American Journal of Science, 1874 (3), 8, p. 188.
[2] Leeds, Annals Lyceum of Natural History, New York, 1878, p. 193.
[3] Schlösing, Chemisches Centralblatt, 1869, p. 678.
[4] von Jolly, Wiedemanns Annalen, N.F., 1879, 6, p. 520.

TABLE 33.—*Determinations of oxygen made by von Jolly.*

Date.	Barometer.	Wind.	Oxygen.	Date.	Barometer.	Wind.	Oxygen.
1877.	*mm.*		*p. ct.*	1877.	*mm.*		*p. ct.*
June 13	714.03	W.	20.53	Oct. 21	723.0	E.	20.84
June 18	717.7	N.	20.95	Oct. 23	710.6	NW.	20.84
June 24	716.8	NE.	20.73	Oct. 27	721.5	N.	21.01
June 27	718.7	NE.	20.65	Oct. 31	714.2	W.	20.85
June 31	718.1	NE.	20.69	Nov. 2	724.1	NE.	20.91
July 3	716.9	E.	20.66	Nov. 10	718.2	SE.	20.56
July 17	713.1	S.	20.64	Nov. 13	707.0	W.	20.67
July 19	713.9	SW.	20.56	Nov. 20	708.9	NW.	20.65
July 27	719.9	NE.	20.75				
Oct. 12	715.7	E.	20.78	Min.	714.03	W.	20.53
Oct. 14	720.9	NW.	20.86	Max.	721.5	N.	21.01
Oct. 15	719.3	E.	20.83	Av ...	——	.....	20.75
Oct. 16	723.3	E.	20.75				

Since these results agree with the variations found earlier by him, von Jolly concludes that the highest oxygen percentage is accompanied by a polar wind. He opposes Regnault's contention of an approximately constant composition of the air and in conclusion makes the following interesting and important statements:

Ob von Jahr zu Jahr die Schwankungen stets in gleichen Grenzen erfolgen, und ob im Mittel der Sauerstoffgehalt in jedem Jahre der gleiche ist, wird erst durch eine ausgedehntere Beobachtungsreihe sich feststellen lassen. Zunächst ist es wahrscheinlich, dass ebenso wie die Dauer der Polar—und Aequatorströme an gleichem Orte nicht jedes Jahr die gleiche ist, auch kleine Differenzen im mittleren Sauerstoffgehalte sich von Jahr zu Jahr werden geltend machen. Auch wird man aus den Beobachtungen zweier Jahre schliessen dürfen, dass trotz der reicheren Vegetationsdecke südlicherer Breitegrade die Oxydationsprozesse (vielleicht in Folge der höheren Temperatur) die Reduktionsprozesse überwiegen, während umgekehrt der reichere Gehalt an Sauerstoff der Polarströme ein Zurücktreten der Oxydationsprozesse gegen die der Reduktion für die nördlicheren Gegenden ausdrückt.

A series of analyses of air samples taken at the observatory in Palermo in 1879 were reported by Macagno,[1] who was one of the first observers to use potassium pyrogallate systematically in air-analysis. (See table 34.)

TABLE 34.—*Results of analyses of atmospheric air made by Macagno.*

Date.	Oxygen.	Carbon dioxide.	Date.	Oxygen.	Carbon dioxide.
1879.	*p. ct.*	*p. ct.*	1879.	*p. ct.*	*p. ct.*
Feb. 20	20.879	0.021	May 31	20.017	0.033
Feb. 28	20.891	.048	June 10	20.894	.041
Mar. 10	20.715	.025	June 20	20.918	.043
Mar. 20	19.994	.025	June 30	20.915	.043
Mar. 31	20.888	.022	July 10	20.977	.020
Apr. 10	20.910	.021	July 20	20.984	.076
Apr. 20	20.880	.064	July 31	20.899	.039
Apr. 30	20.898	.045	Aug. 10	20.910	.028
May 10	20.913	.005	Aug. 20	20.888	.030
May 20	20.902	.049	Aug. 31	20.895	.039

[1] Macagno, Chemical News, 1880, **41**, p. 97.

Average results for February, March, April, and May (with rainfall) were for oxygen, 20.717 per cent, and for carbon dioxide, 0.033 per cent. For June, July, and August (without rainfall) the average results were for oxygen, 20.920 per cent, and for carbon dioxide, 0.039 per cent.

Macagno emphasizes the low percentage of oxygen found during the sirocco wind, the extremely low percentages on March 20 and May 31 being due to this cause. The percentages of oxygen obtained during the sirocco were as follows:

1879.	per cent	1879.	per cent
March 20	19.994	May 29	20.021
March 21	20.008	May 30	20.032
March 22	20.064	May 31	20.017
April 15	19.998		

Commenting on these results, Macagno writes:

> Here we have seven determinations of the most important element of air during that singular wind with its heat and dryness,[1] rendering so troublesome the medium in which we are always bathed, and in all cases the want of oxygen is very evident.

Simultaneously, but independently of von Jolly, E. W. Morley,[2] of Cleveland, engaged in the accurate analysis of air with a view to studying the variations in composition and formulating a hypothesis which he hoped would be subsequently verified with an improved apparatus. Morley maintained that the descent of cold air from higher regions brought with it air poorer in oxygen, presupposing the correctness of the Dalton hypothesis. The apparatus[3] used was a modification of that of Frank-

TABLE 35.—*Determinations of oxygen in atmospheric air collected by Morley after sudden depressions of temperature.*

Date.	Average temperature.	Oxygen.		Date.	Average temperature.	Oxygen.	
		First analysis.	Second analysis.			First analysis.	Second analysis.
1878.	°F.	p. ct.	p. ct.	1879.	°F.	p. ct.	p. ct.
Dec. 28	....	20.98	20.96	Feb. 16	26.3	20.95	....
1879				Feb. 20	18.9	20.87	20.87
Jan. 2	7.6	20.91	20.92	Feb. 26	22.3	20.45	20.50
Jan. 2	7.6	20.90	20.89	Feb. 27	12.8	20.77	20.80
Jan. 3	−7.2	20.90	20.91	Mar. 15	22.8	20.88	20.84
Jan. 3	−7.2	20.96	20.97	Mar. 15	22.8	20.84	20.86
Jan. 6	13.5	20.97	....	Mar. 16	25.3	20.92	20.92
Jan. 10	9.6	20.96	....	Mar. 17	24.5	20.89	20.90
Jan. 28	37.4	20.96	....	Apr. 3	25.0	20.77	20.79
Feb. 1	18.5	....	20.96	Apr. 3	....	20.85	20.87
Feb. 1	18.5	20.94	20.94	Apr. 4	27.1	20.80	20.80
Feb. 2	19.8	20.91	20.93	Apr. 4	27.1	20.88	20.85
Feb. 2	19.8	20.82	20.80	Apr. 5	28.2	20.77	20.77
Feb. 15	11.1	20.88	20.86	Apr. 5	28.2	20.86	20.82

[1] During the sirocco wind the relative humidity of air (determined by the psychrometer) is diminished to 30°, 24°, 20°, and even 18°.
[2] Morley, American Journal of Science and Arts, 1879, 18, p. 168.
[3] Morley, loc. cit.; also Amer. Chem. Journ., 1881, 3, p. 1.

land and Ward,[1] in which the hydrogen-explosion method is employed. Most of the samples were analyzed in duplicate, the difference at times being 0.05 per cent. An abstract of his results is given in table 35.

The most noteworthy observations in this series are the extremely low values occasionally found for oxygen. On this point Morley says:

> On Sept. 16, 1878, two very careful analyses of the same sample gave 20.49 and 20.46 per cent of oxygen. * * * Within the time covered by the analyses now published, there were several well-marked great and sudden depressions of temperature, and the figures show the falling off in the proportion of oxygen in the air at these times to be as well marked as the depression of temperature. The deficiency is not proportionate to the depression of temperature; this could not be expected.

In a second communication,[2] Morley reports a very large number of analyses made with even greater care, comparing the results with the meteorological conditions which existed at the time. The investigation extended from January 1, 1880, to April 20, 1881, analyses being made nearly every day except during the vacation months of July, August, and September 1880. Usually duplicate analyses of the same sample were made and occasionally several samples were taken on the same day. For painstaking care and extent the work is marvelously complete. A part of his results are given in table 36, these being fairly indicative of the accuracy of the work, and the agreement of duplicate analyses.

TABLE 36.—*Determinations of oxygen in atmospheric air made by Morley.*

Date.	Oxygen.		Date.	Oxygen.		Date.	Oxygen.	
	First analysis.	Second analysis.		First analysis.	Second analysis.		First analysis.	Second analysis.
1881.	*p. ct.*	*p. ct.*	1881.	*p. ct.*	*p. ct.*	1881.	*p. ct.*	*p. ct.*
Jan. 1	20.949	20.939	Jan. 10	20.966	20.967	Jan. 21	20.948	20.950
Jan. 1	20.936	20.940	Jan. 11	20.957	20.959	Jan. 22	20.938	20.933
Jan. 2	20.954	20.960	Jan. 12	20.963	20.956	Jan. 23	20.955	20.947
Jan. 2	20.952	20.947	Jan. 13	20.958	20.957	Jan. 24	20.959	20.958
Jan. 3	20.959	20.957	Jan. 14	20.957	20.961	Jan. 25	20.952	20.947
Jan. 4	20.954	20.951	Jan. 15	20.960	20.961	Jan. 26	20.969	20.967
Jan. 5	20.958	20.958	Jan. 16	20.952	20.952	Jan. 27	20.959	20.959
Jan. 6	20.956	20.953	Jan. 17	20.959	20.957	Jan. 28	20.953	20.961
Jan. 7	20.958	20.948	Jan. 18	20.950	20.952	Jan. 29	20.960	20.954
Jan. 8	20.946	20.960	Jan. 19	20.956	20.956	Jan. 30	20.968	20.964
Jan. 9	20.954	20.962	Jan. 20	20.958	20.960	Jan. 31	20.960	20.962

While Professor Morley cites numerous instances of meteorological conditions accompanied by decreases in oxygen which are consistent with his hypothesis, there are fully as many days of low oxygen when he admittedly is unable to explain the fall as a result of meteorological change. Furthermore, he repeatedly cites falls in oxygen amounting to but 0.01 per cent as significant. Morley concludes that there is no connection between the deficiencies in oxygen and the direction of the wind at the

[1] Frankland and Ward, Quart. Journ. Chem. Soc. (London), 1854, 6, p. 197.
[2] Morley, American Journal of Science, 1881 (3), 22, p. 417.

time of taking the sample and "that the theory that deficiencies in the amount of oxygen in the atmosphere are caused by the descent of air from an elevation fairly well agrees with the facts." In another paper[1] Morley discusses in detail the improbability of the von Jolly hypothesis.

The experimental researches of Morley and von Jolly stimulated, among other writers, Vogler,[2] who, in a theoretical presentation of the subject, maintains that neither von Jolly's hypothesis nor that of Morley explains the anomalies as well as does the conception of a separation of the gases of the air under conditions of high pressure. During a period of minimum barometer he maintains that the rapidly moving currents of air thoroughly mix the atmosphere, so that there is no difference in the oxygen content, but when there is a period of high barometer the air is quiet and there is a separation of the gases, with a high oxygen content near the earth.

Table 37.—*Determinations of oxygen made in air analyzed by Kreusler.*

Date.	Oxygen.	Date.	Oxygen.	Date.	Oxygen.	Date.	Oxygen.
1883.	*p. ct.*	1883.	*p. ct.*	1883.	*p. ct.*	1883.	*p. ct.*
Jan. 5	20.882	Apr. 2	20.925	July 12	20.927	Oct. 30	20.879
Jan. 7	20.905	Apr. 5	20.881	July 18	20.900	Nov. 2	20.899
Jan. 8	20.927	Apr. 9	20.991	July 25	20.924	Nov. 5	20.888
Jan. 9	20.914	Apr. 19	20.867	July 30	20.945	Nov. 8	20.922
Jan. 11	20.899	Apr. 23	20.923	Aug. 4	20.930	Nov. 12	20.895
Jan. 13	20.925	Apr. 26	20.909	Aug. 7	20.936	Nov. 15	20.909
Jan. 14	20.900	Apr. 30	20.873	Aug. 10	20.906	Nov. 19	20.908
Jan. 17	20.900	May 3	20.896	Aug. 13	20.895	Nov. 22	20.903
Jan. 20	20.886	May 7	20.909	Aug. 17	20.934	Nov. 26	20.918
Jan. 21	20.917	May 10	20.919	Aug. 20	20.910	Nov. 29	20.901
Jan. 22	20.902	May 13	20.912	Aug. 24	20.933	Dec. 3	20.876
Jan. 23	20.884	May 16	20.896	Aug. 29	20.917	Dec. 6	20.900
Jan. 25	20.913	May 21	20.928	Sept. 2	20.886	Dec. 10	20.916
Jan. 26	20.915	May 24	20.914	Sept. 10	20.937	Dec. 13	20.904
Jan. 27	20.912	May 29	20.906	Sept. 14	20.883	Dec. 17	20.936
Jan. 28	20.984	June 1	20.927	Sept. 17	20.923	Dec. 20	20.902
Jan. 29	20.895	June 4	20.918	Sept. 20	20.888	Dec. 24	20.911
Jan. 30	20.914	June 7	20.926	Sept. 24	20.890	Dec. 27	20.907
Jan. 31	20.908	June 12	20.937	Sept. 27	20.985	1884	
Feb. 4	20.926	June 15	20.917	Oct. 1	20.911	Jan. 11	20.937
Feb. 7	20.937	June 18	20.911	Oct. 4	20.916	Jan. 19	20.922
Feb. 10	20.900	June 20	20.894	Oct. 7	20.885	Jan. 23	20.941
Feb. 13	20.909	June 25	20.894	Oct. 11	20.924	Jan. 24	20.914
Feb. 16	20.899	June 28	20.926	Oct. 15	20.928	Jan. 27	20.925
Feb. 19	20.911	July 3	20.906	Oct. 18	20.921	Jan. 30	20.925
Feb. 22	20.895	July 6	20.918	Oct. 22	20.900	Feb. 7	20.936
Mar. 24	20.884	July 9	20.904	Oct. 25	20.916		

By far the most complete collection of the literature on the composition of atmospheric air thus far published is to be found in the admirable article by Kreusler.[3] Using a eudiometer similar to that employed by

[1] Morley, American Journal of Science, 1881 (3), **22**, p. 429.
[2] Vogler, Chemisches Centralblatt, 1882 (3), **13**, p. 556.
[3] Kreusler, Landwirtschaftliches Jahrbücher, 1885, **14**, pp. 305–378. This article, although published in a somewhat inaccessible place, has been most helpful in preparing the material for this memoir. I have freely drawn upon the material Professor Kreusler has collected and wish to express here my appreciation of his paper.

von Jolly, Kreusler made a series of analyses of atmospheric air in Bonn. These observations covered the whole year, averaging about 8 or 9 experiments each month, March excepted. About the middle of the year, certain improvements were made in the apparatus. His results are abstracted in table 37.

As a result of his experiments, Kreusler found that the oxygen varied from 20.867 to 20.991 per cent as the extreme limits, but with certain exceptional cases eliminated, the variations were from 20.88 to 20.94 per cent. The 99 observations in the year 1883 gave an average result of 20.911 per cent. The average values for each month were as follows:

	p. ct.		p. ct.		p. ct.
January	20.910	May	20.910	September	20.913
February	20.911	June	20.917	October	20.909
March	......	July	20.918	November	20.905
April	20.910	August	20.920	December	20.906

The slightly higher values found during the warmer months are explained by Kreusler as being due to the assimilative activity of vegetation.

In referring to earlier analyses, Kreusler considers all experiments in which the variations were under 0.1 per cent as normal results, those between 0.1 and 0.15 abnormal, and those over 0.15 per cent as most abnormal. Of the 1025 observations that he has been able to find in the literature which are comparable, but 15 can be classified under the head of "abnormal" and 22 under the head of "most abnormal." The observations of von Jolly in Munich in 1878 play an important rôle in this subdivision, for his results give 12 normal, 3 abnormal, and 6 most abnormal; Kreusler points out that while in the case of the other observations 97.2 per cent are normal and only 1.2 and 1.6 are abnormal and most abnormal, respectively, the experiments of von Jolly give but 57 per cent normal, with 14.3 and 28.6 per cent, respectively, as abnormal and most abnormal. Obviously, therefore, von Jolly has found much greater variations than all the other observers combined, and consequently Kreusler takes exceptions to his conclusions. Furthermore, the average oxygen content found in von Jolly's experiments was 20.75 per cent, which is very much lower than both the earlier and later observations.

After considering the errors in von Jolly's experiments, Kreusler discusses the anomalous observations of Brunner, Lewy, Regnault and Lewy, Liebig, Macagno, and Morley, and says in conclusion:

Ich glaube hiermit den Nachweis geliefert zu haben, dass die ja lange Zeit herrschend gewesene, neuerdings aber mehrfach wieder in Zweifel gezogene Annahme einer innerhalbenger Grenzen konstanten Zusammensetzung der atmosphärischen Luft thatsächlich noch zu Recht besteht, insofern alle entgegengesetzten Beobachtungen bis jetzt nicht genügend verbürgt scheinen.

In testing his extremely complicated apparatus for gas-analysis, Geppert[1] made a number of air-analyses, employing the hydrogen ex-

[1] Geppert, Die Gasanalyse und ihre physiologische Anwendung nach verbesserten Methoden, Berlin, 1885, p. 96.

plosion for the determination of oxygen. A sufficiently large sample was taken to eliminate the errors incidental to working with minute quantities of gas such as would be obtained from blood; the results given in table 38 were obtained for the percentage of oxygen. The extremely low value of 20.68 is attributed by the author to a defect in the particular eudiometer used for this single determination. The author points out that if one wishes to make exact gas-analyses it is desirable to test the eudiometer previously with normal air.

TABLE 38.—*Percentages of oxygen determined on atmospheric air by Geppert.*

Series 1.	Series 2.	Series 3.	Series 4.	Series 5.	Series 12.
p. ct.	*p. ct.*	*p. ct.*	*p. ct.*	*p. ct.*	*p. ct.*
20.910	20.848	20.885	20.948	20.88	20.96
20.928	20.863	20.904	20.912	20.91	20.97
20.929	20.837	....	20.912	20.93	20.97
....	....	....	....	....	20.68
....	....	....	....	....	20.91

Contemporaneously with Morley and von Jolly, but working entirely independently, Hempel, employing potassium pyrogallate as the absorbing agent, began a research on the composition of the air.[1] In 1877 he found, as the result of many analyses, differences so great as to be explainable only on the ground of imperfect technique. Subsequent development of apparatus and method yielded a procedure so accurate that duplicate analyses of each day's sample did not vary from one another by more than 0.02 per cent. On five different days in the fall of 1877 he found 20.89, 20.76, 20.96, 20.91, and 20.90 per cent of oxygen, respectively. In 1879, analyses were made in April and May as follows:

	p. ct.		p. ct.		p. ct.
Apr. 24	21.16	Apr. 27	20.83	Apr. 30	20.83
Apr. 25	20.91	Apr. 28	20.87	May 1	20.82
Apr. 26	20.92	Apr. 29	20.70	May 3	20.55

By means of the improved apparatus, an interesting comparative series of analyses was made, samples of air being collected in July 1883, simultaneously by Professor Hempel in Dresden and Professor E. Hagen on the steamer between Liverpool and New York, all samples being taken at 8 a. m. The results are given in table 39.

TABLE 39.—*Determinations of oxygen in atmospheric air, collected at sea and in Dresden.*

Date.	At sea.	Dresden.	Date.	At sea.	Dresden.
1883.	*p. ct.*	*p. ct.*	1883.	*p. ct.*	*p. ct.*
July 22	20.94	20.93	July 27	20.87	20.92
July 23	20.80	20.92	July 28	21.09	20.97
July 24	20.88	20.86	July 29	20.91	21.01
July 25	20.91	20.91	July 30	21.01	20.95
July 26	20.95	....			

[1] Hempel, Berichte der deutschen chemischen Gesellschaft, 1885, 18, p. 267.

Using identically the same apparatus, Oettel in Hempel's laboratory determined each day the carbon dioxide and oxygen of Dresden air from October 12, 1884, to December 24, 1884. Oettel's results are expressed in the form of a curve not easily reproduced, but table 40 shows his results from November 8 to 18. The duplicate analyses permit an estimate of the accuracy of the method he used. The figures also show the general extent of the variations he observed in the oxygen and carbon-dioxide content of the atmosphere.

TABLE 40.—*Determinations of oxygen in Dresden air, made by Oettel.*

Date.	Oxygen and carbon dioxide.	Carbon dioxide.	Date.	Oxygen and carbon dioxide.	Carbon dioxide.
1884.	*p. ct.*	*p. ct.*	1884.	*p. ct.*	*p. ct.*
Nov. 8	{ 20.84 20.85	0.036 .037	Nov. 14	{ 20.81 20.78	0.049 .054
Nov. 9	{ 20.87 20.89	.039 .041	Nov. 15	{ 20.82 20.79	.038 .041
Nov. 10	{ 20.88 20.86	.050 .055	Nov. 16	{ 20.80 20.83	.0416 .0430
Nov. 11	{ 20.90 20.91	.0389 .0391	Nov. 17	{ 20.86 20.84	.040 .037
Nov. 12	{ 20.74 20.75	.040 .044	Nov. 18	{ 20.92 20.92	.040 .044
Nov. 13	{ 20.77 20.75	.044 .048			

A few months later Hempel, in defending the use of potassium pyrogallate from the criticism raised by Kreusler,[1] published further experiments on air.[2] In one sample of air he reports, as the result of four determinations in which carbon dioxide and oxygen were collectively absorbed, 20.936, 20.938, 20.938, and 20.938 per cent, respectively—an agreement that is striking.

TABLE 41.—*Determinations of oxygen in atmospheric air, made by Hempel.*

Date.	Oxygen and carbon dioxide.	Carbon dioxide.	Average oxygen.	Date.	Oxygen and carbon dioxide.	Carbon dioxide.	Average oxygen.
1885.	*p. ct.*	*p. ct.*	*p. ct.*	1885.	*p. ct.*	*p. ct.*	*p. ct.*
Feb. 3	{ 20.960 20.955	0.035	20.920	Feb. 11	{ 20.950 20.944	0.037	20.910
Feb. 6	{ 20.970 20.980	.035	20.939	Feb. 12	{ 20.965 20.968	.035	20.932
Feb. 7	{ 20.945 20.960	.035	20.917	Feb. 13	{ 20.958 20.974	.036	20.930
Feb. 8	{ 21.001 20.991	.034	20.962	Feb. 14	{ 20.932 20.946	.034	20.905
Feb. 9	{ 20.969 20.979	.034	20.940	Feb. 15	{ 20.975 20.971	.035	20.938
Feb. 10	{ 20.961 20.958	.034	20.926				

Beginning with February 3, 1885, Hempel made duplicate analyses of air nearly every day until March 28. The results for the first half of

[1] Kreusler, loc. cit.
[2] Hempel, Berichte der deutschen chemischen Gesellschaft, 1885, **18**, p. 1800.

February are given in table 41 as illustrative of the accuracy of his work and of the magnitude of the fluctuations experienced by him.

An examination of all of his results shows a minimum of 20.877 per cent, a maximum of 20.971 per cent, with a difference of 0.094 per cent, and an average of 20.93 per cent of oxygen. Hempel points out that his results compare favorably with those of Kreusler, who found 20.911 per cent, and of Morley, who obtained 20.949 per cent, each investigator using a wholly different method.

Obviously to three such skilled experimenters as Morley, Kreusler, and Hempel, the uncertainty regarding the general question as to the constancy, or lack of constancy, of the oxygen content of the air was somewhat disconcerting, and it is not surprising that we find them in 1886 engaging in a coöperative investigation. Morley in Cleveland, Kreusler in Bonn-Poppelsdorf, and Hempel in Dresden collected samples at the same time, making due allowances for geographical location. In addition, Hempel secured the aid of Pusinelli, who took samples in Para, Brazil, and of Schneider, who simultaneously took samples at Tromsö in Norway. Thus the times for collecting were:

Cleveland	8^h 18^m a.m.	Dresden	2^h 38^m p.m.
Para	10 31 a.m.	Tromsö	3 00 p.m.
Bonn	2 12 p.m.		

Kreusler,[1] who made the determinations with his glowing copper-wire eudiometer, published his results independently shortly before Hempel's paper[2] appeared.

Kreusler abates somewhat his criticism of the pyrogallic-acid method, but still adheres to von Jolly's copper eudiometer. His results need not here be reproduced in full, as they are in part incorporated with those of Hempel and Morley in table 42. Kreusler found percentages of oxygen ranging from 20.907 to 20.939, substantiating his earlier findings and belief that the oxygen fluctuations, in spite of changes in meteorological conditions, are small. The average is 20.922 per cent, which is a little higher than the average of his earlier results, *i. e.*, 20.911. Hempel's summary of the complete investigation includes the results of both Kreusler and Morley. A specimen set of records from April 1 to April 11, 1886, will serve to show both the agreement of duplicates and the variations experienced in various places. The samples from Tromsö, Dresden, and Para were all analyzed alike, in that both oxygen and carbon dioxide were simultaneously absorbed. Oxygen alone was determined in the samples collected in Bonn and Cleveland.

The Tromsö analyses usually showed an agreement within 0.01 per cent on the same day; on several occasions the difference was 0.03 per cent, but the average for each day showed a fluctuation ranging from 21 per cent down to 20.90 per cent. It should be borne in mind that the

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[1] Kreusler, Berichte der deutschen chemischen Gesellschaft, 1887, **20**, p. 991.
[2] Hempel, *ibid.*, p. 1864.

results obtained from the Tromsö samples were for oxygen plus carbon dioxide and not for oxygen alone.

TABLE 42.—*Comparative study of the oxygen content of air, made by Kreusler, Hempel, and Morley.*

Date.	Oxygen and carbon dioxide.						Oxygen.		
	Tromsö.		Dresden.		Para.		Bonn.	Cleveland.	
	Found.	Average.	Found.	Average.	Found.	Average.	Found.	Found.	Average
1886	*p. ct.*	*p. ct.*	*p. ct.*	*p. ct.*	*p. ct.*	*p. ct.*	*p. ct.*	*p. ct.*	*p. ct.*
Apr. 1	20.95	20.94	20.94	20.94	20.91	20.91	20.93	20.90	20.90
	20.93	....	20.93	....	20.91	....	....	20.90	
Apr. 2	20.94	20.94	20.96	20.96	....	....	20.93	20.93	20.93
	20.94	....	20.96	....	....	....	....	20.93	
Apr. 3	....	....	20.93	20.93	....	....	20.91	20.91	20.92
	....	....	....	....	....	....	....	20.92	
Apr. 4	20.94	20.94	20.95	20.95	20.91	20.91	20.93	20.93	20.93
	....	....	20.95	....	20.92	....	....	20.93	
Apr. 5	20.95	20.95	20.93	20.94	20.92	20.93	20.92	20.94	20.94
	20.94	....	20.94	....	20.93	....	....	20.94	
	....	....	20.94						
Apr. 6	20.97	20.97	20.92	20.93	20.95	20.95	20.92	20.93	20.93
	20.97	....	20.94	....	20.95	....	....	20.93	
Apr. 7	20.96	20.96	20.89	20.90	20.93	20.93	20.92	20.93	20.93
	20.96	....	20.90	....	20.92	....	....	20.93	
Apr. 8	....	....	....	....	20.90	20.90	20.91	20.91	20.91
	....	....	....	....	20.90	....	....	20.91	
Apr. 9	20.97	20.96	20.91	20.91	20.96	20.96	20.90	20.93	20.93
	20.95	....	20.91	....	20.96	....	....	20.93	
Apr. 10	20.96	20.96	20.93	20.93	20.95	20.95	20.93	20.93	20.93
	20.95	....	20.92	....	20.95	....	....	20.93	
Apr. 11	....	....	20.92	20.92	20.91	20.91	20.92	20.92	20.93
	....	....	20.91	....	20.91	....	....	20.93	

The Dresden samples showed very slight variations, the results for the same day usually being very close, and commonly exactly alike. In one instance only was there a difference of 0.02 per cent. The average for different days ranged from 20.96 per cent down to 20.88 per cent; the maximum and minimum did not coincide with those for Tromsö.

For the Para samples the agreement for individual days was likewise very close, although in all not so many samples were analyzed. The agreement was within 0.01 or 0.02 per cent, the difference in no instance being more than 0.02 per cent. The average for the day showed fluctuations from 20.99 to 20.86 per cent.

The analyses made in Tromsö, Dresden, and Para, therefore, since they all represent the content of oxygen plus carbon dioxide, are directly comparable with one another, the averages being respectively: For Tromsö, 20.946 per cent; for Dresden, 20.928 per cent; and for Para, 20.923 per cent. On the supposition that the carbon-dioxide content remained on the average 0.03 per cent, and assuming that it was somewhat higher in the day period than in the night, Hempel computed the average oxygen content by deducting 0.03 per cent, and found for Tromsö, 20.92 per cent;

for Dresden, 20.90 per cent; and for Para, 20.89 per cent, respectively. In the same month, therefore, the oxygen content in the neighborhood of the poles was somewhat higher than in the neighborhood of the equator.

In the oxygen values found in Bonn, only a single observation for each day was given, or possibly these figures represent the average for each day. They varied from 20.94 to 20.90 per cent.

The values for the Cleveland samples, which also represent the oxygen content alone, showed usually an exact agreement between duplicates on the same day, and in only a few instances was there a discrepancy of 0.01 per cent. The averages ranged from 20.95 to 20.90 per cent.

The total averages for these two places are: For Bonn, 20.922 per cent; for Cleveland, 20.933 per cent.

The total average value obtained by the analysis of 203 different air samples, collected in five different places, and analyzed by three different methods, is 20.91 per cent of oxygen.

On an expedition to Cape Horn to observe the transit of Venus, Muntz and Aubin[1] made analyses of air taken at Orange Bay, using the eudiometer of Regnault and Reiset as modified by Schloesing. Their results are given in table 43. The authors conclude that the average oxygen percentage in the air taken near Cape Horn is less than the value found by Regnault in Paris, but essentially that found in different parts of the world; they believe, however, that the proportions of oxygen and nitrogen are subject to variations which are within the narrow limits established by Regnault.

TABLE 43.—*Determinations of oxygen in atmospheric air, made by Muntz and Aubin.*

Date.	Oxygen.	Date.	Oxygen.	Date.	Oxygen.
1883.	*p. ct.*	1883.	*p. ct.*	1883.	*p. ct.*
May 10	20.86	May 17	20.97	July 22	20.90
May 11	20.92	May 18	20.85	July 22	20.95
May 12	20.93	May 19	20.88	July 29	20.89
May 13	20.89	May 19	20.72	Aug. 1	20.78
May 14	20.95	May 22	20.87	Aug. 2	20.79
May 15	20.90	May 24	20.84	Aug. 2	20.83
May 16	20.72	July 5	20.83		

Phosphorus as an absorbent of oxygen again made its appearance in air-analysis in the hands of Ebermayer,[2] who analyzed air from forests in 1885. He found in free atmospheric air 20.82 per cent of oxygen.

Breslauer[3] analyzed air in Brandenburg at least once a month, sometimes as frequently as two or three times each month from January to December. As an average of 20 analyses he gives 20.934 per cent, with a minimum of 20.895 and a maximum of 20.955 per cent.[4]

[1] Muntz and Aubin, Comptes rendus, 1886, **102**, p. 421.

[2] Ebermayer, Fortschritte a. dem Gebiete der Agrikultur-Phys., **9**, p. 229; abstracted in Chemisches Centralblatt, 1886, **17**, p. 770.

[3] Breslauer, Die chemische Beschaffenheit der Luft in Brandenburg a. H., Berlin, 1886.

[4] Breslauer, Deutschen Medizinal-Zeitung, 1885, **6**, p. 1.

In connection with his research on the influence of the ingestion of food on metabolism, Magnus-Levy[1], in Zuntz's laboratory, described a new form of gas-analysis apparatus in which phosphorus is used to absorb oxygen. To demonstrate the accuracy of his apparatus he reports the determinations of the oxygen percentages in a series of 16 air-analyses, as follows:

p. ct.	p. ct.	p. ct.	p. ct.
20.90	20.90	20.73?	20.88
20.93	20.88	20.81	20.86
20.89	20.97?	20.90	20.90
20.89	20.82	20.90	20.88

Leduc[2] in 1890, recognizing the discrepancy between the results of Regnault on the one hand and of Dumas and Boussingault on the other, sought to explain the difference on the grounds of slight errors in Regnault's determinations of the densities of the gases. One year later Leduc,[3] having questioned the accuracy of absorbing oxygen by copper, inasmuch as nitrogen combined with the hydrogen of the reduced copper, used Brunner's method, in which the oxygen is absorbed by phosphorus, and weighed both the air and the nitrogen remaining. Two experiments carried out with the greatest care gave 23.244 and 23.203 per cent of oxygen by weight, or 21.024 and 20.987 per cent by volume, respectively. The author obtained the same results by determining the densities of nitrogen and oxygen.

Wanklyn and Cooper,[4] using the pyrogallic-acid method, obtained on three samples 20, 20.8, and 20.5 per cent of oxygen, respectively. By explosion with hydrogen they obtained 21.34, 20.94, and 21.34 per cent of oxygen.

Using an alkaline ferroso-tartrate solution for an absorbent, de Koninck[5] found as the mean of four determinations 21.00 per cent of oxygen.

Laulanie[6] in 1894 published the description of a eudiometer in which the oxygen was determined by absorption with phosphorus. He claimed very accurate results, with a constant oxygen percentage of 20.9.

Using a modified Bunsen apparatus, Schaternikow and Setschenow[7] made analyses of laboratory air in Moscow, and report 12 analyses of outdoor air. The oxygen percentage ranged from 20.874 to 21.036, with an average of 20.962 per cent.

By passing a measured amount of air and nitric oxide through hydriodic acid, Kreider,[8] in New Haven, Connecticut, determined the free iodine thus liberated by means of 1/10 normal arsenious acid by titration. He gives a series of results with outdoor air on two samples collected over

[1] Magnus-Levy, Archiv für die gesammte Physiologie, 1894, **55**, p. 1.
[2] Leduc, Comptes rendus, 1890, **111**, p. 262.
[3] Leduc, Comptes rendus, 1891, **113**, p. 129.
[4] Wanklyn and Cooper, Air analysis, London, 1890, p. 35.
[5] de Koninck, Chemical News, 1891, **64**, p. 45.
[6] Laulanie, Archives de Physiologie, 1894, **26**, p. 739.
[7] Schaternikow and Setschenow, Zeitschrift für physikalische Chemie, 1895, **18**, p. 56.3
[8] Kreider, Zeitschrift für anorganische Chemie, 1896, **13**, p. 423.

water; 11 analyses made on the same sample of air gave percentages of oxygen varying from 20.91 to 21.19, with an average of 21.08, and on another day 6 analyses of the same sample of air gave percentages varying from 20.96 to 21.03, and averaging 20.99. The author also reports two analyses of air by pyrogallic acid, showing 20.93 and 20.88 per cent of oxygen, respectively.

Employing a reaction first utilized by Winkler[1] to determine the oxygen dissolved in water, Chlopin[2] utilized the interaction between manganous salt and oxygen in the presence of potassium iodide to determine the oxygen content of gaseous mixtures by titration. The results of a series of analyses of the air taken in the court of the Hygienic Institute in Dorpat are given in table 44.

Table 44.—*Results of analyses of outdoor air, made by Chlopin.*

Date.	Oxygen.	Date.	Oxygen.
1897.	*p. ct.*	1897.	*p. ct.*
Feb. 25	20.86	Apr. 2	21.08
Mar. 4:		Apr. 10	20.97
Sample *a*	20.87	June 1	20.87
Sample *b*	20.89	June 2	20.91
Mar. 8:		June 5	20.84
Sample *a*	20.88		
Sample *b*	20.94	Average	20.905
Mar. 13	20.95		
Mar. 19	20.90		

A second paper by Chlopin[3] reports analyses of outdoor and room air, but does not indicate which are those for outdoor air.

Samojloff and Iudin,[4] describing a method of gas-analysis in which a modified Bunsen apparatus was used, have published a considerable number of analyses of outdoor air. Using explosion with hydrogen to determine the oxygen, they found 20.97, 20.97, 20.96, 21.00, 20.99, 20.99, 21.01, 20.99, 20.96, 20.92, 20.97, and 20.98 per cent. Two analyses with pyrogallic acid gave 20.91 and 21 per cent of oxygen, respectively.

In 1902, Krogh, of Copenhagen, on a voyage to the island of Disko, west of Greenland, latitude 70° north, undertook a number of analyses of atmospheric air. While the prime object of his research was to study the carbon-dioxide tension in natural waters and especially in the sea, these determinations were combined with direct analyses of the atmospheric carbon dioxide and oxygen. The analyses were made with a Haldane apparatus, the burette of which contained only 10 c. c. The accuracy is given as 0.005 to 0.01 per cent and the numerous double determinations generally agree within these limits.[5] The extensive series of oxygen de-

[1] Winkler, Berichte der deutschen chemischen Gesellschaft, 1887, **21**, p. 2843. Also *ibid.*, 1889, **22**, p. 1764.
[2] Chlopin, Archiv für Hygiene, 1899, **34**, p. 71.
[3] Chlopin, Archiv für Hygiene, 1900, **37**, p. 329.
[4] Samojloff and Iudin, Le Physiologiste Russe, 1901, **2**, p. 171.
[5] Krogh, Meddelelser om Groenland, 1904, **26**, p.333.

terminations obtained at this time are reported in a second article discussing the abnormal carbon-dioxide percentage of the air in Greenland, and the general relations between atmospheric and oceanic carbon dioxide.[1] On 22 days samples of air were taken from a number of different places in Greenland, 47 determinations of oxygen being made. Excepting one observation of 20.84 per cent, which was attributed by the author to a possible analytical error, the results exhibit variations from 20.92 to 21.015 per cent. Omitting the very low value of 20.84 per cent, the average of the determinations is 20.960 per cent. Of particular significance is the fact that analyses made on the same samples showed extremely high values for carbon dioxide, ranging at times from 0.025 to 0.07 per cent.

In a private communication from Dr. Krogh, he reports that a series of experiments made by him in Greenland in 1908 showed oxygen percentages ranging from 20.895 to 20.980, with an average of 20.945. The unusually high carbon-dioxide percentages of former years were not obtained, although two observations gave 0.055 per cent. Dr. Krogh also writes that in 1907 and 1908 Dr. Lindhard of Copenhagen made observations in northeast Greenland (Denmark Haven) using the identical modified Pettersson apparatus described by Dr. Krogh in a former paper. He reports that Lindhard's results would be liable to about 0.001 per cent error, and they agreed perfectly with those found by himself on the west coast. Lindhard generally found about 0.035 per cent of carbon dioxide, but on one or two days it was below 0.03 per cent, and on 5 days out of 23, 0.04 per cent or more. The maximum value found was 0.062 per cent.

Dr. Krogh, commenting upon his own determinations of oxygen, writes that they may have an error of several hundredths of a per cent, as the absolute accuracy may be much affected by dirt accumulating in the burette and by variations and gradual displacement of the contained water. He says: "I do not think that it is at all possible to determine oxygen with great absolute accuracy except by analyzing dry and in a perfectly clean burette."

It should be borne in mind that Dr. Krogh's original investigation dealt simply with the carbon-dioxide tensions in air and in water, and the oxygen determinations were quite incidental; likewise, the oxygen determinations in 1908 were made in connection with experiments with the respiration apparatus for determining the gaseous exchange of Eskimos. As one of the foremost investigators in gas-analysis, Krogh's experiences are doubly valuable.[2]

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[1] Krogh, Meddelelser om Groenland, 1904, **26**, p. 409.

[2] On a recent trip to Copenhagen, I was accorded the privilege of seeing a new gas-analysis apparatus devised by Dr. Krogh in which the conditions outlined by him above are fully realized. Unfortunately, at the time of going to press with this report, Dr. Krogh has not completed satisfactorily his experiments with this apparatus.

By means of the apparatus described by Atwater and Benedict,[1] Miss Charlotte R. Manning[2] made a number of air-analyses at Middletown, Connecticut, the details of which are given in table 45.

In 1904 Chandler[3] reported a series of analyses made of 50 samples of air collected in the New York subway, the content of oxygen ranging from 20.3 to 20.8 per cent. Determinations were also made of the oxygen in 9 samples of surface air; the results ranging from 20.6 to 20.9 per cent.

TABLE 45.—*Determinations of oxygen in atmospheric air, made at Wesleyan University in Middletown, Connecticut.*

Date.	Direction of wind.	Oxygen.		
		I.	II.	III.
1903.		*p. ct.*	*p. ct.*	*p. ct.*
Nov. 25	W.	20.91	20.92	....
Nov. 27	W.	20.95	21.00	20.93
Nov. 30	SW.	21.09	21.03	....
Dec. 4	NE.	21.05	20.97	20.97
	SW.	21.01	21.00	....
Dec. 5	NNW.	20.97	20.99	....
	NW.	21.01	20.99	....
Dec. 7	W.	20.93	20.92	20.90
	W.	21.01	21.00	....

Pécoul and Gizolme[4] published in 1903 the description of their method of air-analysis, in which they employed a unique absorption apparatus and potassium pyrogallate. They also published the results of an analysis of an air sample collected in Paris at Place Lobau, the percentage of carbon dioxide obtained being 0.03 and of oxygen 20.85.

Utilizing the extremely ingenious manometer and compensating device of his earlier apparatus, Pettersson and Högland[5] so modified this apparatus as to determine not only the carbon dioxide but also the oxygen, using sodium hydrosulphite as the absorbing agent. They report the average of all the oxygen determinations made by them in Stockholm in October, November, and December 1889 as 20.940 per cent. Unfortunately, although the authors promised further details and additional results, no published report has as yet appeared; nor did a personal visit to Stockholm result in obtaining further information.

That this method was extremely promising was foreseen by Jaquet,[6] who, in connection with the development of his most ingenious respiration apparatus, felt the imperative need of exact oxygen determinations. Employing an apparatus modeled after the design of Pettersson, but using

[1] Atwater and Benedict, Carnegie Institution of Washington Publication No. 42, 1905.
[2] Unpublished data from laboratory note-book.
[3] Chandler, The air of the subway, New York, 1904 (privately printed).
[4] Pécoul and Gizolme, Annales d'Observatoire Municipal (Observatoire de Mont Souris), Paris, 1903, 4, p. 184.
[5] Pettersson and Högland, Berichte der deutschen chemischen Gesellschaft, 1889, **22**, p. 3324.
[6] Jaquet, Verhandlungen der naturforschenden Gesellschaft in Basel, 1904, **15**, p. 252.

potassium pyrogallate as the reagent, Jaquet analyzed a number of samples of outdoor air and reports the results in support of his contentions regarding the accuracy of his apparatus. These are given in table 46.

TABLE 46.—*Results of air-analyses made by Jaquet.*

Sample No.	Carbon dioxide.	Oxygen.
	p. ct.	*p. ct.*
1............	0.02	20.93
2............	.03	20.935
3............	.032	20.928
4............	.032	20.928
5............	.038	20.94
6............	.032	20.94
Average ..	.031	20.934

Staehelin, using the same apparatus as Jaquet, reported in 1907[1] that in 51 analyses of air in Basel the average oxygen content was 20.90 per cent. The average value was found only in 22 samples. Twice the oxygen was less than 20.89 per cent and eight times larger than 20.91 per cent. The extreme values were 20.875 and 20.94 per cent.

Using the gas-analysis apparatus in Basel, Gigon[2] found with potassium pyrogallate that the oxygen content of the air near the laboratory varied between 20.87 and 21.2 per cent. These fluctuations he is inclined to attribute to the fact that the laboratory is in the center of the city and near large factories.

In connection with the use of the Zuntz-Geppert respiration apparatus, many analyses of air have been made and occasionally such analyses are reported. Few have greater interest than those published by Durig and Zuntz[3] in connection with the description of one of their trips into the high Alps.

TABLE 47.—*Results of air-analyses made by Durig and Zuntz.*

Date.	Place.	Carbon dioxide.	Oxygen.
1903.		*p. ct.*	*p. ct.*
Aug. 14	Col d'Olen..................	0.04	20.88
Aug. 19	....Do....................	.03	20.86
Aug. 23	Capanna Margherita.........	.02	20.89
Aug. 31	....Do....................	.02	20.88
Sept. 6	....Do....................	.03	20.87

In 1903 they analyzed free air at Col d'Olen and at the Capanna Margherita on the summit of Monte Rosa. The results are given in table 47. The authors state that these results, which agree with their numerous

[1] Staehelin, Verhandlungen der Naturforschenden Gesellschaft in Basel, 1907, **19**, p. 9.
[2] Gigon, Archiv für die gesammte Physiologie, 1911, **140**, p. 517.
[3] Durig and Zuntz, Archiv für Anatomie und Physiologie, Physiologische Abtheilung, Suppl. Bd., 1904, p. 421.

analyses in Berlin, substantiate the belief that the atmosphere has a constant constitution up to an altitude of 4600 meters.

In a private communication Professor Durig writes that in the two expeditions in 1903 with Zuntz and in 1906[1] with Frau Durig and others, he made over 100 analyses of air. The percentage of oxygen was always between 20.87 and 20.96. On the Teneriffe expedition in 1907 he found from 20.87 to 20.98 per cent—limits almost exactly those experienced in Vienna and on Monte Rosa.

In describing his extremely accurate and ingenious gas-analysis apparatus, Haldane[2] has published the results of a number of air-analyses. Four analyses of the same sample of air gave the following percentages:

Analysis.	Oxygen.	Carbon dioxide.
1............	20.930	0.025
2............	20.926	.030
3............	20.931	.035
4............	20.924	.030
Average	20.928	.030

The author concludes that 20.93 per cent may be taken as the true percentage of oxygen in pure air.

Absorbing the oxygen from dry air by means of heated yellow phosphorus, Watson,[3] working in Guye's laboratory in Geneva, determined the oxygen in air collected in Geneva and on some of the nearby mountains. In describing his method, he includes a few preliminary results which are given in table 48.

TABLE 48.—*Analyses made by Watson of air collected in Switzerland.*

Source of air.	Oxygen.		
	I.	I.	III.
Laboratory, Geneva (alt. 300 m.):	*p. ct.*	*p. ct.*	*p. ct.*
July 11, 1910, 4 p.m.	20.96	20.93	....
July 12, 1910, 5 p.m.	20.98	20.95	....
May 19, 10 a.m.	21.02	21.04	21.03
Saléve (alt. 1300 m.), May 19, 10 a. m.....	20.95	20.93	....
Rochers de Naye (alt. 2045 m.):			
May 19, 10 a.m.	21.02	....	....
May 19, 5^h30^ma.m....................	21.04	....	....

[1] Durig, Archiv für die gesammte Physiologie, 1906, 113, p. 213.
[2] Haldane, in The investigation of mine air, by Foster and Haldane, London, 1905, p. 113. See also, J. S. Haldane, Methods of air analysis, London, 1912, p. 44.
[3] Watson, Journal of the Chemical Society, August, 1911, p. 1460.

SUMMARY OF HISTORICAL DIGEST.[1]

While the earliest studies of the composition of the atmosphere can hardly be considered as giving results of quantitative significance, these researches stimulated greatly the study of chemistry in general and air-analysis in particular, the great interest in the composition of the atmosphere leading to the rapid development of many methods of analyses.

Seldom has a philosophical instrument or a chemical process attracted so much attention as did the eudiometer, which utilized the reaction between nitric oxide and air. Although soon discarded for methods better founded scientifically, the apparatus nevertheless was a ready and portable means for increasing the interest of investigators and diffusing a knowledge of the composition of the air. The successors of this method, *i. e.*, methods involving the use of absorbents like alkaline sulphides or phosphorus, or employing explosion with hydrogen, all of which depended upon volumetric measurements, soon demonstrated the difficulties in air-analysis—difficulties which taxed the ingenuity and the patience of practically all the prominent chemists.

One figure in this early history of air-analysis shines out above all others—that of the scholarly, isolated Scheele. That Scheele may rightly be designated as the pioneer in the study of the chemistry of the air few who examine the literature can deny. His results, while admittedly of no quantitative significance, do nevertheless imply a knowledge of the chemistry of the air, of its composition, and of the possibilities of change in its composition, which was expressed no more clearly by other writers many years later.

Eudiometric observations were exclusively relied upon during the first 50 years of the development of air-analysis, but later gravimetric methods were introduced by Brunner and Dumas in which the oxygen was absorbed by copper or phosphorus, and was subsequently weighed. Then there followed a return to the hydrogen-explosion method, which was advanced to the highest degree of accuracy by Bunsen, Regnault, Frankland and Ward, and Morley. Meanwhile the interesting method of Liebig, employing an alkaline solution of pyrogallic acid, and the copper eudiometer of von Jolly made their appearance.

In all of these earlier researches we find that while the chemical processes involving the absorption of oxygen from the atmosphere were capable of innumerable refinements, the grossest errors were due to purely

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[1] In compiling the historical material in this book I have been greatly aided by Miss B. Clark, librarian of the William Ripley Nichols Library of the Massachusetts Institute of Technology; and Mrs. Austin Holden, of the Library of the American Academy of Arts and Sciences; and my thanks are especially due to Dr. J. S. Billings and his associate, Dr. Henryk Arctowski, of the New York Public Library. The facilities of the library of the Harvard Medical School, the Library of Congress, and the Surgeon General's Library have also been freely drawn upon.

I am also much indebted to Dr. E. P. Cathcart, of Glasgow, 1911–1912 Research Associate of the Carnegie Institution of Washington, attached to this laboratory, for his painstaking and critical reading of the entire manuscript of this book.

mechanical reasons, chiefly to the solubility of gases in water, the difficulties of physical measurements, the lack of knowledge concerning the physical properties of gases, the inadequate and incorrect calibrations of the glassware then in use, improper temperature control, and the imperfect preparation of the hydrogen—these factors affecting more or less the accuracy of the data obtained with the earlier methods.

As the more popular chemical processes for the determination of oxygen in the air have varied materially—the eudiometric method first being used, then the gravimetric, and finally the eudiometric method again—similarly we find that the prevailing opinion has fluctuated with regard to the constancy or lack of constancy in the composition of the air. When the eudiometer was first used it was firmly believed that the oxygen percentage varied enormously, and, indeed, that the salubrity of any climate was directly proportional to the amount of oxygen present. Just at this time Cavendish, although using an imperfect apparatus, made a remarkable series of experiments, coming to the conclusion that the composition of the air was constant; in other words, that there were no fluctuations that were measurable on his instrument.

Then followed the development of the law of gases and of union by volume, with the measurement of the oxygen and nitrogen in the air as approximately 1 to 4, which led to the belief that the air was a chemical compound, having the formula N_4O. This belief, however, was soon discarded, inasmuch as it was found possible to separate the nitrogen and oxygen by mere physical processes, particularly that of diffusion. Evidence began to be accumulated to demonstrate that the percentage of oxygen in the air was not sufficiently constant to justify the use of the formula N_4O; indeed, there appeared to be considerable variation in the composition of the air. As experimental work progressed, however, the variations began to grow less. In a long series of investigations, covering 50 years, no variations in the oxygen content greater than 0.15 per cent were found, save in desultory observations made under conditions that do not inspire the greatest degree of confidence. The only exception was the interesting research in 1887 of von Jolly in Munich, who, by absorbing the oxygen in his copper eudiometer, found much greater variations than had formerly been obtained. Independently and simultaneously, but employing a somewhat different form of apparatus with the highest grade of technique, Morley in Cleveland found similar results, although the fluctuations were much smaller than those found by von Jolly. Morley's experiments continued over a period of several years, ultimately resulting in the belief that the oxygen content of the air was affected by downward currents, particularly following a sudden drop in temperature. The researches of Morley and von Jolly stimulated further study and were followed by the coöperative investigations of Morley, Kreusler, and Hempel, which showed that under proper control the fluctuations formerly found in part disappeared.

Finally, as an indication of the present-day conception of the composition of the atmosphere, the following, written by F. W. Clarke[1] in 1908, may be cited:

In a roughly approximate way it is often said that air consists of four-fifths nitrogen and one-fifth oxygen, and this is nearly true. The proportions of the two gases are almost constant, but not absolutely so; for the innumerable analyses of air reveal variations larger than can be ascribed to experimental errors. A few of the better determinations are given in the subjoined table [table 49], stated in percentages by volume of oxygen. They refer, of course, to air dried and freed from all extraneous substances.

Some of these variations are doubtless due to different methods of determination, but others can not be so interpreted. Hempel, comparing his analyses of air from Tromsoe, Norway, and Para, Brazil, infers that the atmosphere is slightly richer in oxygen near the poles than at the equator, an inference that would seem to need additional data before it can be regarded as established. The most significant variation of all, however, has been pointed out by E. W. Morley.[2] As oxygen is heavier than nitrogen it has been supposed that the upper regions of the atmosphere should show a small deficiency in oxygen, as compared with air from lower levels; although analyses of samples collected on mountain tops and from balloons have not borne out this suspicion. It is also supposed that severe depressions of temperature, the so-called "cold waves," are connected with descents of air from very great elevations. Morley's analyses, conducted daily from January, 1880, to April, 1881, at Hudson, Ohio, sustain this belief. Every cold wave was attended by a deficiency of oxygen, the determinations, by volume, ranging from 20.867 to 21.006 per cent, a difference far greater than could be attributed to errors of measurement. Air taken at the surface of the earth seems to show a very small concentration of the denser gas, oxygen.

TABLE 49.—*Determinations of oxygen in air, in percentage by volume.*

Analyst.	Locality.	Number of analyses.	Minimum.	Maximum.	Mean.
			p. ct.	*p. ct.*	*p. ct.*
V. Regnault	Paris	100	20.913	20.999	20.960
R. W. Bunsen	Heidelberg	28	20.840	20.970	20.924
R. Angus Smith	Manchester	32	20.78	21.02	20.943
Do.	Mountains of Scotland	34	20.80	21.18	20.970
U. Kreusler	Near Bonn	45	20.901	20.939	20.922
W. Hempel	Dresden	46	20.877	20.971	20.930
Do.	Tromsoe	41	....	21.00	20.92
Do.	Para	28	20.86	....	20.89
A. Muntz and E. Aubin	Cape Horn	20	20.72	20.97	20.864
E. W. Morley	Cleveland, Ohio	45	20.90	20.95	20.933

[1] Clarke, Data of geochemistry, U. S. Geological Survey Bulletin 330, 1908, p. 38.
[2] Morley, American Journal of Science, 1879, 3d ser., 18, p. 168; 1881, 22, p. 417.

PART II.

ANALYSES OF ATMOSPHERIC AIR MADE AT THE NUTRITION LABORATORY.

From the standpoint of pure physiological chemistry, the importance of an exact knowledge of the composition of the air entering the lungs is obvious when one attempts to consider the various means for studying the respiratory exchange. Every living individual is continually taking into the lungs air of a certain composition, which on leaving the lungs has a different composition. By knowing the volume of air passing through the lungs and the change in composition, important deductions with regard to the metabolic processes can be made. Furthermore, in certain lines of physiological experimenting, it is customary to confine a subject inside an air-tight chamber through which a current of ventilating air is passed, the changes in composition of the air inside the chamber being accurately measured. Obviously, here again it is necessary to know the exact oxygen content of the air entering the chamber.

Although recognizing that the evidence thus far accumulated shows slight differences in the percentage of oxygen in the air, experimenters for the most part have been content to assume a constancy in this factor for air supplied to a respiration chamber or entering the lungs through nose-pieces or a mouth-piece in an apparatus requiring special appliances for breathing. Singularly enough, however, while assuming a certain degree of constancy, investigators have been at variance in regard to the value to be assigned for the oxygen content of the air. In examining the literature one finds, even in recent researches, variations in the assumed composition all the way from 20.88 to 20.96 per cent. With the Zuntz respiration apparatus and with the Chauveau and Tissot apparatus, the changes in composition of the air passing through the lungs are very great, so that this difference in assumed composition is not of as great magnitude as it is with other forms of apparatus. For example, air entering the lungs may be assumed to contain 20.93 per cent of oxygen, and determinations of the air leaving the lungs may show an oxygen content of 16.93 per cent, or a difference of 4 per cent. Consequently an error of 0.04 per cent in the assumed composition of the air entering the lungs would only make an error of 1 per cent in the total oxygen determined.

One of the most important and promising methods of studying the respiratory exchange is that elaborated by Professor Jaquet of Basel, and extensively used by both Staehelin[1] in Berlin and by Grafe[2] in Heidel-

[1] Staehelin and Kessner, Charité-Annalen, 1909, **33**, p. 1.
[2] Grafe, Zeitschrift für physiologische Chemie, 1910, **65**, p. 1.

berg. This apparatus is essentially on the Pettenkofer-Voit principle, in that a current of fresh air constantly passes through the chamber. The air leaving the apparatus is analyzed, the change in composition being assumed to have resulted from the metabolic activity of the subject inside the chamber. In his modification of the Pettenkofer-Voit apparatus, Jaquet has included the determination of the oxygen in the outgoing air-current, thus obtaining data regarding the amount of oxygen used, as well as the carbon dioxide produced. With a large ventilation the oxygen deficit may be very small in amount; conversely, the smaller the ventilation, the larger will be the deficit. Unfortunately, most workers with this apparatus, although recognizing the fact that the oxygen deficit should be large rather than small, in practice frequently do not heed it and many experiments have been reported in which it is but 0.50 per cent. Under these conditions, therefore, it can be easily seen that an error in assuming the oxygen content of the incoming air may be of considerable moment, for each 0.01 variation may make a difference of 2 per cent in the determination of the oxygen absorbed. It might further be said at this point, although it is not necessarily germane to this discussion, that the small oxygen deficit so commonly used by workers with the Jaquet apparatus is likewise enormously affected by analytical errors in determining the oxygen in the outcoming air. The Jaquet system is simple, and has many advantages in its favor, but in using it an exact knowledge of the composition of the air entering as well as of that leaving the chamber is of fundamental importance.

A knowledge of the exact oxygen content of the air inside the respiration chamber is also of great importance in using the Regnault-Reiset type of respiration apparatus. For example, assuming that the air in a chamber containing 1000 liters has an oxygen percentage of 20.93, the oxygen content would be approximately 209.3 liters. An error of 0.1 per cent in the determination of the oxygen would therefore result in an error of practically 1 liter in the total amount of oxygen residual in the chamber, so that with an oxygen consumption of approximately 15 liters per hour, the error in the determination of the total oxygen consumption might easily amount to one-fifteenth, or approximately 6 per cent.

One of the most important uses of the determination of the oxygen content of the air in the chamber, however, is not so much to obtain an exact knowledge of the amount of oxygen present as to indicate in an elaborate and complicated apparatus the presence of a leakage of air into or out of the system. This point was brought out in a former publication.[1] In a closed-chamber apparatus, it is obvious that with an initial volume of 1000 liters of air there can be no change in the nitrogen content by virtue of metabolic processes,[2] so that from hour to hour it should re-

[1] Atwater and Benedict, Carnegie Institution of Washington, Publication No. 42, 1905, p. 93.

[2] Krogh, Skandinavisches Archiv für Physiologie, 1906, 18, p. 364.

main essentially the same. If, however, there is a leakage of air out of the system and a consequent replenishment of oxygen to maintain constancy in volume, obviously there would be a loss in nitrogen. On the other hand, if there is a leakage of air into the system, less oxygen will be required to obtain constancy in volume, and the percentage of nitrogen will continually increase. By making, at stated periods, determinations of the nitrogen in the residual air, it is possible not only to detect when there has been a leakage of air into or out of the system, but also from the results obtained to compute easily the magnitude of this leakage.[1] This principle has been used recently by Rolly[2] in making experiments with a small respiration apparatus.

At this point it should be stated that throughout this discussion it is considered for convenience that the air used for the determinations of oxygen is free from water and carbon dioxide. Furthermore, since the proportion of argon and the rarer gases in the atmosphere does not play any rôle in this research, no special recognition is made of the presence of 0.94 per cent of argon. It is therefore assumed that the air consists only of nitrogen and oxygen, and that after the absorption of the oxygen the residual gas is pure nitrogen.

While there are a large number of methods for determining the carbon dioxide produced by the body, the determination of the oxygen consumption is at best a very difficult procedure. When the Regnault-Reiset type of apparatus in this laboratory has been thoroughly tested and shown to be air-tight, air-analyses are unnecessary; nevertheless for long-continued experiments, periodical, accurate determinations of the oxygen in the air residual in the chamber are important. Consequently, the physiological importance of knowing the constancy or lack of constancy in the composition of the air justified the study of this problem by the Nutrition Laboratory.

FUNDAMENTAL ESSENTIALS OF ACCURATE AIR-ANALYSES.

Although the gravimetric determination of oxygen in air was especially successful in the hands of Dumas and Brunner, it is too time-consuming to be practicable for metabolism experimentation, and hence there has been a general trend in the last 30 years toward the volumetric determination of oxygen by absorption with either phosphorus or potassium pyrogallate. An apparatus for the determination of oxygen in physiological laboratories, to be successful and practical, should have first an efficient absorbent for oxygen, *i. e.*, the last traces of oxygen should be readily absorbed; second, no by-products of the chemical reaction should be given off into the residual gas, thereby increasing its volume; third, temperature changes in the apparatus during the process of an analysis should

[1] For an elaboration of this theory and its successful application, see Atwater and Benedict, loc. cit., pp. 88–89, and 93.

[2] Rolly and Rosiewicz, Deutsches Archiv für klinische Medizin, 1911, **103**, p. 58.

be fully compensated or readily corrected; fourth, barometric changes in pressure taking place during an analysis should be fully compensated; fifth, there should be an equal tension in the gas before and after absorbing oxygen in the final measurement; and sixth, the contraction in volume as measured should be due only to the absorption of oxygen.

Absorbents for oxygen.—Of the numerous absorbents for oxygen, including phosphorus, potassium pyrogallate, and, more recently, sodium hydrosulphite, there seems to be but little choice with regard to the completeness of absorption. Although both phosphorus and potassium pyrogallate are affected somewhat by low temperature, when properly handled they absorb oxygen completely. While the same is true of sodium hydrosulphite, certain difficulties in the way of handling this reagent have precluded its general adoption by chemists.[1]

Formation of by-products.—The absorption of oxygen is invariably an oxidative process. Usually the products of oxidation are non-gaseous, particularly when phosphorus and metallic absorbents are used. On the other hand, it has been claimed that in the interaction between oxygen and potassium pyrogallate a small amount of carbon monoxide is formed. This militated greatly against the use of potassium pyrogallate in the earlier stages of its introduction, but in more recent years a study of its composition has led to changes in the general method of using this reagent so that the formation of any measurable amount of carbon monoxide has been practically precluded; hence as satisfactory results can be obtained with potassium pyrogallate as with phosphorus.

Correction for temperature changes.—From the time when the sample of gas is first measured until after the absorption of either carbon dioxide or oxygen and its subsequent measurement, there should be no material alteration in the volume of the gas due to temperature. Modern apparatus corrects for these temperature changes by means of a compensating vessel or pipette of the same size and in the same temperature environment as the vessel used for measuring the sample. Frequently both vessels are immersed in a water-bath which is constantly stirred to secure temperature equilibrium.

Barometric fluctuations.—While usually of slight moment, inasmuch as the analyses can be readily carried out in a few minutes, barometric changes should also be taken into consideration. Particularly is this the case in exact gas-analysis when the period of contact between the air and the various reagents must be longer than in the ordinary technical analysis. In some analyses it may require 30 minutes or more for com-

[1] The use of sodium hydrosulphite, employed by Tobiesen (Skandinavisches Archiv für Physiologie, 1895, **6**, p. 278), has been more recently brought to the attention of physiologists by Durig, of Vienna. (See Biochemische Zeitschrift, 1907, **4**, p. 65.) The necessity for preventing the corrosive action of this reagent on glass has called for a certain technique that is not readily acquired; for example, Durig coats the inside of his pipette thinly with gutta percha. The absorption coefficient of the solution of this reagent is extremely high, but as yet the chemical has not come into general use, although it can now be readily purchased in a pure form.

plete absorption; during this time there may be an appreciable barometric change. Practically all modern gas-analysis apparatus provides for this change in temperature by adjusting the compensating pipette so as to take care not only of the changes in temperature but likewise changes in barometric pressure. Under these conditions it can be safely said that within reasonable limits all changes in temperature and pressure are readily compensated by the modern compensating pipette of the best forms of gas-analysis apparatus.

Tension of aqueous vapor.—The varying percentages of water in samples of air and the differences in tension of the aqueous vapor above the absorbing solutions make it necessary to insure that the tension of gases before and after absorption remains exactly the same. This is best secured in practically all modern gas-analysis apparatus by saturating the gas with water-vapor both before and after absorption. A satisfactory method for this is the placing of a few drops of water upon the surface of the mercury which is ordinarily used as the liquid for inclosing and measuring the sample. Under all conditions, therefore, the gas as measured is saturated with water-vapor at the temperature of the water-bath. If in the compensating pipette both water-vapor and a slight excess of water are present, then the tension of aqueous vapor is exactly the same in the compensating pipette and in the measuring pipette.

Contraction in volume as a measure of the oxygen absorbed.—The most difficult condition in gas-analysis apparatus is to make sure that the contraction in volume as measured is due only to the absorption of oxygen. The usual procedure in measuring the gas is to read the top of the mercury meniscus; obviously, this reading gives not only a measurement of the gas to be analyzed, but of the water-vapor, and also of the liquid water used to insure constancy in the tension of aqueous vapor. The absorption of the gas to be measured changes the level of the mercury, raising it materially; it is assumed that all of the liquid water adhering to the walls of the tube is removed by the mercury as it rises, and that when the mercury meniscus is again read the decrease in volume is due only to the absorption of gas, the volume of liquid water present in the tube above the mercury remaining essentially unchanged. The difficulties experienced in proving this assumption have been practically insuperable, and it has been necessary to resort to a reading of the water meniscus, which is at best very unsatisfactory. Fortunately for purposes of comparison, when essentially the same gas—as atmospheric air, for instance—is analyzed day after day, it is possible to arrange the conditions so as to make the amount of water adhering to the walls of the tube practically constant as the level of the mercury changes. Theoretically, therefore, the best method for analyzing gases is to measure them absolutely dry both before and after absorption in a perfectly dry and clean pipette over absolutely dry and clean mercury. These conditions Dr. Krogh has succeeded in securing in his new gas-analysis apparatus, which unfortunately has not as yet been described.

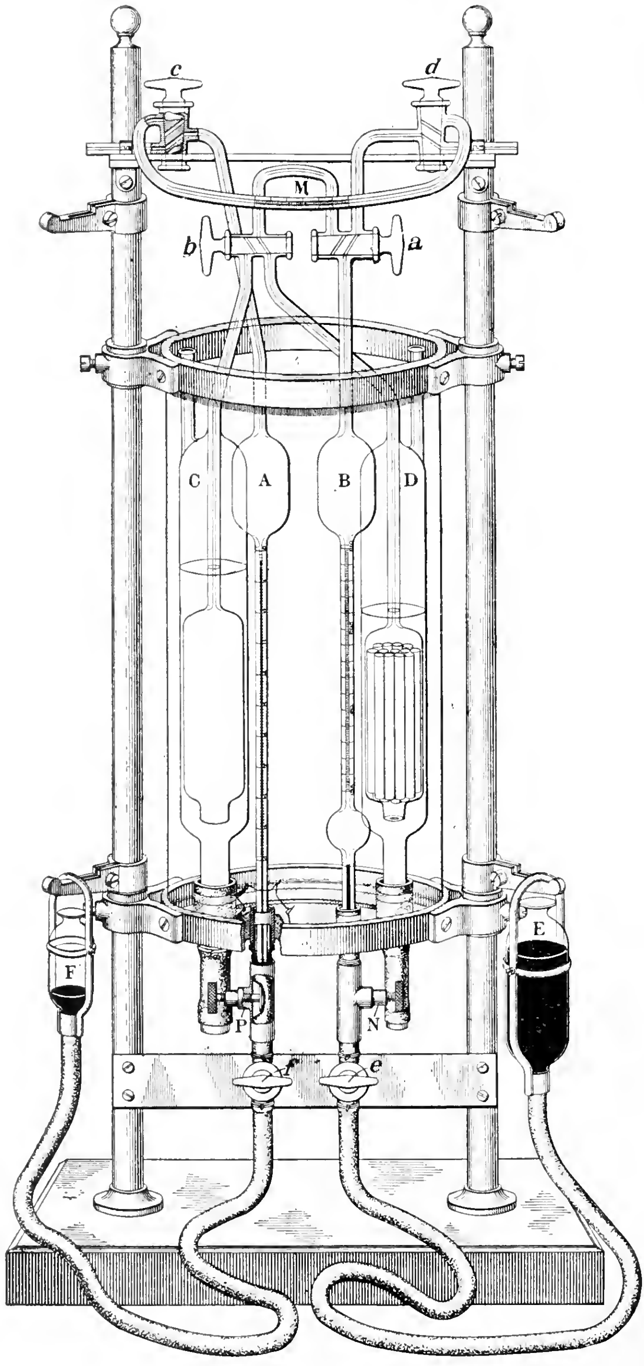

FIG. 1.—Sondén air-analysis apparatus.

The two pipettes *A* and *B*, and the reagent containers *C* and *D*, are immersed in water in the glass tank. Stop-cocks *a*, *b*, *c*, and *d*, permit intercommunication of all parts. Cabron-dioxide percentages are read directly on *A*, and oxygen percentages directly on *B*. Mercury reservoirs *F* and *E* are connected with pipettes *A* and *B* respectively. The manometer *M* aids in securing equal tension in *A* and *B*.

APPARATUS AND TECHNIQUE USED IN THIS RESEARCH.

The importance of securing the highest degree of accuracy in these analyses led to a critical examination of all the forms of gas-analysis apparatus of unusual accuracy now in use. Special attention was given to the apparatus of Haldane,[1] Chauveau,[2] and Sondén-Pettersson.[3] After a careful personal examination had been made of practically every form of exact gas-analysis apparatus in existence, it appeared that the potentialities for exact analysis were greatest with the Sondén apparatus. Accordingly I visited Stockholm to make arrangements for securing such an apparatus, but on my arrival was much discouraged to find that none thus far constructed was sufficiently exact for the research proposed. Through the geniality and interest of Dr. Klas Sondén, however, I was able to spend considerable time with him in discussing the conditions to be met; as a result, he designed and superintended the construction of the apparatus herein to be described, which, we believe, fulfills perfectly all of the conditions outlined except the last, *i. e.*, constancy in volume of the liquid water above the mercury.

Since Dr. Sondén had previously spent a great deal of time in experimenting with the hydrogen method for determining oxygen and the results had been unsatisfactory, it was decided to use, as the absorbing reagent, a strong solution of potassium pyrogallate, potassium hydroxide being used to absorb carbon dioxide. To insure thoroughly controllable temperature conditions, the entire apparatus, including both the two measuring pipettes and the containers for the reagents, is immersed in a water-bath, nothing but capillary tubing being exposed to the room temperature. The apparatus is constructed entirely of glass, and neither the reagent nor the gas is in contact with any other material. The gas volumes are measured over mercury to avoid the solubility of the gases in water, and a few drops of water above the mercury in the measuring pipette insure saturation with water-vapor at the temperature at which the gases are measured.

In using the apparatus a volume of air is first measured, the temperature, pressure, and tension of aqueous vapor being exactly equal to a confined volume of air in a compensating pipette. The air sample is then passed into a strong solution of potassium hydroxide by means of which the carbon dioxide is absorbed. The gas is next returned to the original measuring-vessel and the apparent volume arbitrarily adjusted so as to be the same as before the absorption of the carbon dioxide. There is then a slightly decreased pressure of the confined air due to the volume of car-

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[1] Foster and Haldane, The investigation of mine air, London, 1905. See, also, J. S. Haldane, Methods of air-analysis, London, 1912.

[2] Chauveau's apparatus is described in detail by Tissot, Traité de physique biologique, **1**, pp. 709–723.

[3] Pettersson, Zeitschrift für analytische Chemie, 1886, **25**, pp. 467 and 469; Pettersson and Palmquist, Berichte der deutschen chemischen Gesellschaft, 1888, **21**, p. 21–29; Sondén, Zeitschrift fur Instrumentenkunde, 1889, **9**, p. 472.

bon dioxide absorbed. The volume of the air in the compensating pipette is also adjusted to exactly the same pressure and temperature as that in the measuring-vessel, and by measuring the apparent increase in volume of the air in the compensating-pipette, a direct measure of the carbon dioxide absorbed is obtained. The carbon-dioxide-free air is now passed into the potassium pyrogallate to absorb the oxygen. When the air is again returned to the measuring-pipette, the volume is adjusted so that the tension of the residual gas (nitrogen and argon) is exactly the same as the tension of the gas in the compensating-pipette. The amount of contraction in volume may then be directly read as the percentage of oxygen in the air.

DETAILED DESCRIPTION OF THE APPARATUS.

A somewhat diagrammatic representation of the various parts of the apparatus is given in fig. 1; the apparatus as actually in use is shown in the frontispiece. The main features of this apparatus are two calibrated measuring-pipettes *A* and *B;* two reagent containers *C* and *D;* a delicate manometer *M*, and a series of glass stop-cocks permitting intercommunication between all parts.

The whole apparatus is substantially mounted upon a heavy block of marble. The pipettes and reagent containers are immersed in a glass tank filled with water, which is supported at the bottom by a metal ring support firmly fastened to two nickel-plated uprights (81 cm. high), while a similar ring holds the upper part. In the bottom of the glass tank are four holes, through which the ends of the various pipettes and reagent containers pass, these passages being made water-tight by rubber connections. The water in the tank is stirred by allowing a current of air to bubble through it. Under these conditions, therefore, the temperatures in the apparatus are uniform throughout, and while a thermometer is suspended in the water-bath, the temperature readings made with it are not essential.

The two measuring-pipettes *A* and *B*, the two reagent reservoirs *C* and *D*, and the manometer *M* are connected by capillary tubing and glass stop-cocks, so that all five members are fused together into one whole. Stop-cock *a* connects pipette *B* either with stop-cock *b*, which controls the entrances to the two analytical reagent reservoirs, or with stop-cock *d*, which, in turn, connects with either the outdoor air or with the right side of the manometer *M*. Stop-cock *c* connects pipette *A* with either the outside air or with the left side of the manometer. Stop-cocks *f* and *e* at the bottom provide communication between the leveling reservoirs *F* and *E* and their respective pipettes *A* and *B*. The best quality of stout-walled rubber tubing should be used for connecting the leveling bulb with the stop-cocks *f* and *e*. This is important, since we find that many kinds of rubber tubing contaminate the mercury, so that a thin coating of sulphide, which interferes seriously with the accurate reading of the meniscus level, forms on the top.

Since the changes in the level of the mercury in pipette A are slight (these changes corresponding to the carbon-dioxide percentages of normal air) the leveling bulb F is not usually moved. On the other hand, the leveling bulb E is hung alternately on the upper and lower hooks in order to expel air from pipette B into the solution in either C or D, or out into the air at the completion of the analysis. Minor changes in level of the mercury in the two graduated pipettes are produced by pressure on the rubber tubing with the delicate screw-cocks P and N. By shutting the glass stop-cock f below and screwing in the cock P, pressure can be produced against the rubber tubing so as arbitrarily to adjust at will the level of mercury in the capillary portion of A. A similar adjustment of the mercury level in pipette B may also be made by means of the screw-cock N. In the manometer M a small drop of light petroleum oil serves as an index. When the stop-cocks c and d are removed so that there is atmospheric pressure on each side, this globule should stand in the exact center of the manometer if the apparatus is properly leveled. All stop-cocks are well ground, perfect in fit, and lubricated by a thin layer of mutton tallow. The two calibrated pipettes A and B may be designated respectively the compensating and the measuring pipettes, although measurements are actually made in both.

Compensating pipette.—The compensating pipette is used not only for the final adjustment of the volume of gas in the measuring pipette B, but also for reading directly in its lower graduated portion the percentage of carbon dioxide. The volume of this pipette from the zero mark to the glass stop-cock is 60 cubic centimeters. The graduations demand a special discussion. In all measurements made with this pipette, the gas in both A and B is under definite, though slight, decrease in tension. If the volume of gas in the measuring pipette has been decreased one-thousandth by the absorption of carbon dioxide by the potassium hydroxide, to adjust the air in the compensating pipette to the same tension, the volume of air must be expanded one-thousandth by lowering the mercury a certain amount in the graduated portion of the tube. In the graduation of this pipette, therefore, due cognizance has been taken of the alteration in pressure in the pipette B. The graduations are so arranged as to make the instrument direct reading, the level of the mercury in pipette A indicating the percentage of carbon dioxide in the air sample.

This instrument was primarily designed to study the percentage of oxygen in the air-content or the ventilating current of a respiration chamber. Under these conditions the carbon dioxide may at times be nearly 1 per cent of the air and the deficiency in oxygen approximately the same. The pipette A is so constructed that percentages of carbon dioxide as great as 1 per cent can be measured. Each small division indicates 0.01 per cent and tenths of divisions are readily estimated by the eye, so that records may be obtained with three significant figures when the percentage of carbon dioxide is greater than in normal air.

For the purpose of this discussion, however, we have to deal only with small percentages of carbon dioxide—never over 0.08—and the special extended graduation of this pipette is only of incidental interest. The variations usually found in the carbon-dioxide content of outdoor air are so small that all adjustments of the mercury-level can be made by the adjusting screw P without disturbing the leveling-bulb F.

Measuring pipette.—The measuring pipette B has two bulbs, the zero mark being placed slightly below the lower bulb. Between the two bulbs is a constricted portion which is graduated and represents that part of the pipette corresponding to from 19.5 to 21.0 per cent of the total volume. This constriction favors the accurate determination of oxygen, since after the gas is absorbed from a sample of air and is again drawn into the pipette, the mercury-level must be raised a sufficient amount to correspond to the volume of oxygen absorbed. This is usually between 19.5 to 21.0 per cent in experiments with the respiration chamber, and for outdoor uncontaminated air is generally not far from 20.940 per cent. The graduations are such that each scale division corresponds to 0.01 per cent, and hence direct readings may be accurately made to 0.001 per cent. To avoid errors in parallax, the graduation marks on both pipettes completely circle the glass. The total content of pipette B is 60 c. c. A few drops of water are placed in both pipettes A and B and the air is thus continually saturated with water-vapor.

The upper end of each pipette is connected by capillary glass tubing to the various stop-cocks, while the lower end passes through a hole in the bottom of the glass reservoir and is there connected with the adjusting screws P and N, the stop-cocks f and e, and the leveling-bulbs F and E, respectively. Special water-tight closures are necessary where the end of the pipette passes through the glass. These are shown in detail in fig. 1.

After the absorption of oxygen, the level of the mercury in pipette B indicates the percentage of oxygen in carbon-dioxide-free air. When ordinary outdoor air with a carbon-dioxide content of but 0.030 per cent is to be considered, it matters but little, so far as the expression of the percentage of oxygen is concerned, whether the air is carbon-dioxide-free or not, since in one case the proportion would be 20.93 c. c. of oxygen in 100 c. c. of air and in the other 20.93 c. c. in 100 c. c. − 0.03 c. c., or 99.97 c. c. of carbon-dioxide-free air; thus the percentage would not be measurably affected. When, however, there may be 0.8 per cent of carbon dioxide in air taken from a respiration chamber, it becomes a matter of some moment whether the percentage is of carbon-dioxide-free or of carbon-dioxide-containing air.

After the absorption of the carbon dioxide, the mercury-level in the compensating pipette is so adjusted that the air in this vessel is under slightly decreased tension—the decrease in tension being equivalent to the volume of the carbon dioxide absorbed. The final adjustment of the

gas in the measuring pipette likewise produces a corresponding decreased tension. As the pipette is graduated in percentages, it obviously makes no difference whether the gas measured is at atmospheric or less than atmospheric pressure, provided the residual gas is at the same pressure. For this reason, then, when the level of the mercury in the measuring pipette *B* is adjusted after the oxygen is absorbed, no change is made in the level of the mercury in the compensating pipette *A*. The reading for the oxygen, therefore, represents the percentage of oxygen in carbon-dioxide-free air.

Reagent containers.—To insure rapid and efficient absorption, the reagent should be contained in a vessel capable of exposing a relatively large area of reagent to the gas. Since the relation between the area and the volume of gas depends in large part upon the amount of gas to be absorbed, in the case of carbon dioxide, of which no more than 1 per cent is ever present, the area may be very much less than with oxygen of which over one-fifth is absorbed. The forms of reagent containers found most advantageous for this type of apparatus are shown as *C* and *D* in fig. 1. As will be seen, the general structure of both vessels is the same, the notable difference being that *D* contains a large number of short glass tubes which increase greatly the absorbing surface. To prevent the tubes from falling out, the opening at the bottom is somewhat more constricted than in *C*. Each container is so constructed that when filled with the reagent the level inside and out is the same; special marks not only on the inner capillary tube but also around the outer glass envelope of the chamber aid in introducing the proper amount of reagent and in setting the level of the reagent in the capillary. A short length of glass tubing fused to the chamber projects above the level of the water in the tank and, being open to the air, insures atmospheric pressure on the outer surface of the reagent. This tube serves to introduce the various reagents for absorbing the gases to be determined. The lower ends of both chambers project through holes in the glass bottom of the tank, the same precautions for water-tight closure observed in the case of the pipettes *A* and *B* being also here taken.

REAGENTS USED.

The solution for absorbing carbon dioxide.—The solution for absorbing the carbon dioxide is prepared by dissolving 2400 grams of stick potassium hydroxide in 1750 c. c. of water. After the solution becomes cold it is decanted to remove all sediment, and the reservoir *C* is filled through the tube at the top. This is best accomplished by inserting a 20 cm. length of small-sized glass tubing in the open tube and attaching a funnel to it by means of a short bit of rubber tubing. This elongated funnel conducts the reagent well down into the chamber and avoids choking the passage with the somewhat viscous liquid. The level of the liquid inside and out should be essentially the same, the usual height being shown in

fig. 1. Care should be taken to prevent dust from entering the tube or liquid, as it is liable to accumulate on the inside of the reservoir and ultimately cause difficulty in reading the exact height of the liquid in the capillary tubing.

The solution for absorbing oxygen.—Shortly after Liebig announced his discovery of the fact that potassium pyrogallate absorbed oxygen quantitatively, the criticism was raised by Calvert, Boussingault, and Cloez[1] that potassium pyrogallate, when reacting with oxygen, gave rise to the formation of a certain amount of carbon monoxide, the evolution of this gas naturally vitiating the results obtained by this method of analysis. Several years later a further caution was published by Hempel to the effect that one should not use potassium hydroxide "purified by alcohol" in the preparation of the potassium pyrogallate.[2] In this defense of the use of the pyrogallate solution, he also pointed out that if proper attention was given to the concentration of the solution there need be no fear of the evolution of carbon monoxide.

When the formulas for preparing this solution are examined, it is found that the main differences noted are in the proportion of water present. When "a 60 per cent solution of caustic potash" is stated, one immediately has to determine what is meant by "a 60 per cent solution." Even when the weight of potassium hydroxide is given in the formula, difficulty is experienced owing to the differences in water-content of the substance, stick potassium hydroxide frequently containing as much as 25 per cent of water. Haldane's formula alone obviates this difficulty, as he requires a fully saturated solution of potassium hydroxide with a specific gravity of 1.55. Earlier experience with Haldane's formula, however, showed that with a low room-temperature the material solidified; and with so delicate an apparatus as that of Sondén it seemed undesirable to introduce a reagent that might solidify and possibly burst the glass container.

Since the prime object of this research was a comparative study of the oxygen content of the air, and since certain fundamental defects in the apparatus prevented deductions regarding the exact absolute value, we modified slightly Haldane's solution as follows:

A solution of potassium hydroxide was prepared by dissolving 500 grams of stick potassium hydroxide, not purified by alcohol, in 250 c. c. of water. Usually the specific gravity of the resulting solution was 1.55. During the progress of this research, several shipments of stick potassium hydroxide were used, and the varying water-content of the chemical is shown by the fact that it was frequently necessary to add more potassium hydroxide to bring the solution to the desired density. To 135 c. c. of this saturated solution was added a solution of 15 grams of pyrogallic acid

[1] Calvert, Comptes rendus, 1863, **57**, p. 873; Cloez, Comptes rendus, 1863, **57**, p. 875; Boussingault, Comptes rendus, 1863, **57**, p. 885.

[2] Hempel, Berichte der deutschen chemischen Gesellschaft, 1887, **20**, p. 1865.

in 15 c. c. of distilled water. By means of the funnel and tube, the mixed solutions were then carefully introduced into chamber *D*. One such charge of potassium pyrogallate was found to be sufficient to make approximately 30 air-analyses.

This solution takes up oxygen rapidly and has a high absorptive capacity. It has been assumed that since the solution was so much more concentrated than Hempel's, his assertion that no carbon monoxide was developed with his weaker solutions held true in this case also, particularly as Haldane states that with his extremely concentrated solution no traces of carbon monoxide are found. Furthermore, certain evidence here presented seems to support this view. When a known sample of air is analyzed a number of times, the percentage of oxygen at the beginning of the series does not differ from that found at the end, even when as many as 30 analyses are made with the one charge of potassium pyrogallate. It seems reasonable to suppose that if carbon monoxide were formed, a somewhat different amount would be produced after the first, second, or third analysis than after the twenty-eighth or twenty-ninth. On the other hand, it is not impossible that in the production of carbon monoxide there may be an extremely small quantitative relationship between the oxygen absorbed and the disintegration of the pyrogallic acid, so that the carbon monoxide given off may remain strictly proportional to the amount of oxygen consumed. Since in each of these analyses exactly the same amount of oxygen is absorbed, there still may be a slight constant factor present; consequently, it is necessary to take into consideration the fact that in all of these analyses there may be traces of carbon monoxide produced. In that case the tendency would be to make the percentage of oxygen slightly too small. Although throughout the whole research a slightly modified Haldane solution was used, subsequent experiments with the Haldane formula show a somewhat larger oxygen percentage. This increased percentage may be due to two causes: (1) the actual absorption of more oxygen, or what is more probable, (2) the formation of less or no carbon monoxide. It remains a fact, nevertheless, that the solution as used is without question suitable for a comparative study of the oxygen percentage of the atmosphere.

PLAN AND METHODS OF RESEARCH.

The report of the research carried out with this apparatus may be subdivided into several parts as follows:

(1) The main study of the comparative oxygen-content of uncontaminated outdoor air under all conditions as to wind direction and strength, temperature, cloud formation, barometer, and weather, including rain, snow, fog, and mist.

(2) A study of the influence of the temperature of the reagent upon its absorptive power.

(3) An examination of samples of air collected on the North Atlantic Ocean between Montreal and Liverpool, and between Genoa and Boston.

(4) Analyses of air obtained from the top of Pike's Peak.

(5) Analyses of air taken in the crowded streets of Boston.

(6) Analyses of air taken in the Boston and New York subways.

(7) An experimental research with various absorbents for oxygen.

Before proceeding to a description of the routine of air-analysis with this apparatus, a discussion of the method of procuring samples of uncontaminated outdoor air is advisable. By far the greater number of analyses were made of air collected near the laboratory, and a permanent installation was made to secure convenient and accurate sampling of air. It is unnecessary at this point to describe the methods of sampling employed when samples were taken at some distance from the laboratory.

METHOD OF COLLECTING OUTDOOR AIR.

As the laboratory is located near a large power-house, it was feared that in spite of all precautions there would be a contamination of the atmosphere due to the products of combustion from the large furnaces. On the other hand, as the prevailing winds are from the southwest and the power-house is north of the laboratory, it seemed probable that during the prevailing winds the contamination should not be perceptible. In order to provide for a possible variation in composition on two sides of the building, arrangements were made for taking samples on both the east and west sides. The sampling arrangements are as follows:

A standard ⅛-inch brass pipe (7 mm. internal and 10 mm. external diameter) was extended out from the west wall of the laboratory, 4.8 meters from the ground and at a distance of 2.2 meters from the wall. The end was pointed downward so as to prevent clogging by water, ice, or dirt. This pipe was then brought into the laboratory, conducted to the sink near the gas-analysis apparatus, and a water-suction pump so connected as to suck continuously a current of air from outdoors through the pipe. The intake tube of the gas-analysis apparatus was attached to the air-pipe, so that it was possible to have a continuous stream of fresh outdoor air passing by the analysis apparatus. Similarly, a second pipe was carried out from the east side of the building at the same distance from the ground as the pipe on the west side. This pipe was also con-

nected with the gas-analysis apparatus, so that by turning a valve the water-suction pump could be connected with either the west or the east pipe and fresh outdoor air drawn from either side of the building at will. In all analyses care was taken to have the suction pump in full operation for several minutes before taking the sample, thus insuring a complete sweeping out of the pipe by fresh outdoor air. With all analyses simultaneous records have been made of the weather, the direction and strength of the wind, the outdoor temperature, and the barometer.

METHOD OF USING THE APPARATUS AND RESULTS OBTAINED.

The best procedure in the use of this apparatus is by no means obvious from an inspection of its construction; furthermore, as errors appeared in the technique and in the apparatus, the routine has been altered fundamentally on several occasions. Inasmuch as the results first obtained are so completely in harmony with many of those of the earlier investigators, it seems advisable to give our entire series here, even though we know that the results of the first two years are open to objection, owing to slight errors which disappeared as the routine became more perfected.

While the investigation was started primarily to study the oxygen-content of the outdoor air, it was necessary to determine beforehand the carbon dioxide, since an alkaline absorbent for oxygen was employed; hence practically all the analyses are accompanied by simultaneous determinations of the carbon dioxide in the air. In the especially exact apparatus designed by Sondén and Pettersson, the carbon dioxide is determined to the third or fourth significant figure, but as the amounts of carbon dioxide that were to be used in our apparatus might at times reach 1 per cent, it was impossible to secure this degree of fineness in the calibration of the carbon-dioxide pipette, hence readings can be taken only to one-thousandth of 1 per cent. Consequently, since other methods are better adapted for securing accurate carbon-dioxide determinations, little stress has been laid upon the determinations made in connection with this research, although they are probably accurate to within 0.002 in all cases. At one time during the research it was found that the potassium hydroxide reagent chamber *C* was broken, so it became temporarily necessary to absorb simultaneously the carbon dioxide and oxygen; hence for a short period the percentages represent the percentage of oxygen plus that of carbon dioxide. As soon as possible the reagent chamber was repaired and the research was then continued in the usual way.

FIRST ROUTINE, AND RESULTS OBTAINED.

The earlier results in this series are especially interesting as indicating how it is possible by constancy in routine to secure duplicate results on practically all samples. Furthermore, it is interesting to note that if the research had been discontinued at the end of the second year, the results could easily have been taken as verifying completely those of the earlier investigators, who showed that fluctuations in the oxygen content of the atmosphere are to be expected, slight though they may be.

The apparatus described was first set in order in the latter part of February 1909. After considerable preliminary experimenting with room air and with air from a respiration chamber, a series of analyses of outdoor air was begun on April 5, 1909. The first routine employed for determining the carbon dioxide and oxygen is as follows:

Outline of first routine.—It is necessary in the first place to make sure that all the capillary tubes communicating with the different reservoirs are filled with nitrogen and not with air. For this purpose a blank analysis is made in which quantitative accuracy is not required. In making this analysis, the air in the apparatus is first passed into the potassium pyrogallate several times until thorough absorption of both carbon dioxide and oxygen is assured; it is then allowed to flow into the potassium hydroxide and repeatedly drawn back and forth by means of the leveling bulb *E* until the air in all of the capillary tubes is replaced by nitrogen, the air being intermittently sent into the potassium pyrogallate to absorb the slight traces of oxygen picked up in its passage through the capillary tubing. The level of the potassium hydroxide in the capillary tube is then brought to a definite point by lowering the mercury in the pipette *B*, the final adjustment being made by the screw-cock *N*; a decreased tension is thus produced which raises the reagent to the desired mark. When this point is reached the stop-cock *b* is turned 180 degrees to communicate with the chamber *D*. We now have pure nitrogen in the capillary tube leading from the potassium hydroxide reservoir to the stop-cock *b*. Since all the other capillaries are likewise filled with pure nitrogen, pressure is applied at screw-cock *N* to bring the potassium-pyrogallate solution to a definite mark on the capillary tube before shutting off the stop-cock *b*. After turning stop-cock *a* 180 degrees, the excess of nitrogen is then expelled through the stop-cock *d* by means of the leveling bulb *E*.

Between the stop-cock *d* and the pipe coming from the outside of the laboratory is a three-way stop-cock, one side of which is opened to the room air. When taking the sample of air for analysis, this three-way stop-cock is so turned as to allow direct communication between the gas-analysis apparatus and the sampling pipe through which a suction pump draws a current of outside air. Under these conditions, by lowering the mercury reservoir *E*, mercury runs out of the pipette *B* and air is drawn in through the capillary stop-cock *d*. The leveling bulb is again raised and the pipette repeatedly swept out by pure air. When a thorough and accurate sweeping out of the nitrogen is insured and the pipette is full of uncontaminated outdoor air, the sample is ready to be measured. The mercury is finally lowered to a mark somewhat below the zero mark on the pipette. The suction pump is then stopped and the three-way stop-cock between the gas-analysis apparatus and the sample pipe (not shown in either figure) turned so as to communicate directly with the room air. By raising the level of the mercury to the zero mark on the bottom of the pipette *B*, a slight amount of air is expelled and the

level is set exactly at zero by the fine adjusting screw N. The stop-cock c is then turned so that the compensating pipette A communicates directly with the room air, and by means of the finely threaded adjustment screw P, the level of the mercury in A is also brought to the zero point. Under these conditions, therefore, the gas in both pipettes is at the same temperature and pressure. To test this the stop-cocks c and d are simultaneously and *cautiously* turned and the two reservoirs A and B placed in communication with the manometer; there should be no movement of the oil-drop on the scale, thus indicating constancy in temperature and barometric conditions. The stop-cocks c and d are again turned so as to cut off the manometer, and the sample is ready for analysis.

The gas is first sent into the potassium hydroxide to absorb the carbon dioxide. This is done by turning the stop-cock a 180 degrees and subsequently turning stop-cock b so as to allow the air to enter the capillary leading to C. It is next slowly passed into the potassium hydroxide twice by raising and lowering the mercury leveling-bulb E. The air is then drawn back into B, the level of the reagent is again set, and the level of the mercury in the pipette B is brought down to the original zero-mark. Under these conditions there is a slightly diminished pressure in the pipette B, due to the decrease in volume it has sustained by the absorption of the carbon dioxide; consequently, before connecting pipette A to the manometer, the pressure of the air inside A, which is now acting as the compensating vessel, must be somewhat decreased. This decrease in pressure is obtained by lowering the mercury column by an amount which is estimated as being approximately the percentage of carbon dioxide in the air. For ordinary outdoor air this is not far from 0.03 per cent. Under these conditions, therefore, when the stop-cocks c and d communicating with the manometer are turned there will be a slight deflection of the oil globule on the scale to the right or to the left, if the pressure is greater in either A or B. For example, if the movement of the petroleum globule is toward the right, it signifies that the pressure in the pipette A is greater; accordingly, it is necessary to lower the mercury in A until the petroleum drop is exactly in the center. When the manometer shows that the temperature and pressure are the same in both pipettes, a direct reading of the percentage of carbon dioxide may be obtained by noting the fall of the mercury level in A.

To obtain a second reading, the manometer stop-cocks are again turned 90 degrees, and then, by properly turning the stop-cocks a and b, the air is once more sent into the potassium-hydroxide solution. The level of the reagent is again set and after communicating with the manometer the reading is taken. The second reading is usually identical with the first, as the amount of carbon dioxide to be absorbed is extremely small.

At this point the carbon dioxide has been completely removed from the gas in the apparatus, but the capillary tube between the stop-cock b and the level of the potassium hydroxide now contains air instead of nitrogen.

By properly adjusting the stop-cocks *a* and *b* the air sample is slowly sent into the potassium pyrogallate pipette and allowed to remain one minute. After being drawn back and forth twice, it is left over the potassium pyrogallate for another minute, again drawn back and forth twice, next sent to the potassium hydroxide pipette three times, and finally into the potassium pyrogallate three times. When the air leaves each separate pipette for the last time the level for the potassium hydroxide and the potassium pyrogallate respectively are exactly set. Under these conditions there will be a marked difference in the level of the mercury in the pipette *B*, owing to the absorption of the oxygen. In adjusting the level of the mercury in this pipette, instead of drawing it to the zero point, it is brought back until it remains in the upper part of the graduated portion of the pipette. If outdoor air is being analyzed, and the composition is known with considerable exactness, it can usually be set not far from 20.9. Then by communicating with the manometer, and noting whether the oil index moves to the right or to the left, the mercury in the pipette *B* may be raised or lowered as necessary, without altering in any way the level of the mercury in the pipette *A*, until a position is finally obtained which indicates constancy in temperature and pressure conditions exactly like those of the air in the compensating pipette *A*. A reading of the percentage of oxygen is now taken. After turning the manometer stop-cocks, the air is sent into the potassium pyrogallate three times after each reading, and readings are taken until they agree within 0.002 of each other.

The routine outlined was followed with practically no modification from April 5 up to Nov. 3, 1909. The details of an analysis made on April 5 at 11^h45^m a. m. and carried out with this routine are given in table 50.

TABLE 50.—*Results obtained on sample of outdoor air with first routine, April 5, 1909, 11^h45^m a. m.*

Reading.	Carbon dioxide.	Oxygen.
	p. ct.	*p. ct.*
First	0.029	20.893
Second	0.031	20.911
Third	....	20.923
Fourth	....	20.929
Fifth	....	20.929

Results with first routine.—The total results for the first stage in the development of this method, namely, from April 5 until November 3, 1909, are given in table 51. *It should be noted that these results are not of selected analyses, but include the records of every analysis made during this time, including both good and bad.* In the analyses from May 28 to June 3 it was necessary to absorb carbon dioxide and oxygen simultaneously, owing to the fracture of the potassium-hydroxide chamber *C* previously referred to. An examination of the data shows that on the whole there is no material difference between the analyses made of air taken from the

TABLE 51.—*Analyses of outdoor air made at the Nutrition Laboratory.*[1] *Series I.*

Date.	Time.	Temperature.	Barometer.	Wind.	Weather.	West side. Carbon dioxide.	West side. Oxygen.	East side. Carbon dioxide.	East side. Oxygen.
1909.		°C.	mm.			p. ct.	p. ct.	p. ct.	p. ct.
Apr. 5	11h45m a.m.	....	764.10	Light SW	Pleasant	0.031	20.929	0.029	20.920
						.032	20.921	.028	20.941
Apr. 6	4 00 p.m.	16.4	761.35	E.	Do.	.028	20.920	.029	20.880
Apr. 8		11.0	758.50	SW. gale	Do.	.026	20.921	.028	20.921
						.029	20.922	.026	20.931
Apr. 9	11 00 a.m.	8.3	756.50	SE.	Rain	.030	20.918	.030	20.921
						.027	20.919	.030	20.919
Apr. 10	11 00 a.m.	6.8	760.65	W.		.030	20.920	.031	20.920
						.027	20.921	.029	20.920
Apr. 12	5 00 p.m.	11.0	774.50	S	Pleasant	.029	20.920	.030	20.921
						.030	20.920	.029	20.921
Apr. 17	10 00 a.m.	13.7	767.50	S		.029	20.901	[2].030	20.931
	12 00 noon	12.1	767.15	S.		.030	20.911	.032	20.902
Apr. 19		23.7	752.50	SW		.031	20.921	....	....
Apr. 20		8.5	765.35	NE.		.032	20.921	.029	20.920
						.030	20.922	....	.....
Apr. 21	10 00 a.m.	6.8	769.90	E.		.031	20.920	.030	20.922
Apr. 22		14.0	756.30	W.	Pleasant	.031	20.921	.030	20.920
Apr. 23		14.7	760.30	N.		.031	20.920	.030	20.920
Apr. 28	11 00 a.m.	10.9	760.00	W.	Pleasant	.032	20.901	.032	20.902
						.032	20.902	....	....
Apr. 29		13.3	770.50	N.	Do.	.030	20.919	.029	20.919
Apr. 30		2.7	763.65	E.	Rain	.030	20.921	....	....
						.032	20.920	....	....
May 1		6.1	753.50	N.	Rain	.030	20.921	.031	20.920
May 3		11.0	766.60	SW.	Pleasant	.028	20.922	.028	20.921
May 8		....	....			.028	20.920	.034	20.920
						....	.....	.032	20.920
May 10		23.3	760.50	SW.	Pleasant	.028	20.911	.028	20.910
May 12		21.9	764.85	W.	Do.	.029	20.919	.032	20.918
May 13		23.2	764.00	SW.		.029	20.921	.030	20.920
May 14		26.0	757.75	W.		.031	20.920	.029	20.919
May 17		10.1	761.00	E.	Rain	.028	20.920	.029	20.919
May 18		....				.030	20.912	....	....
May 20		13.0	769.65	E.	Pleasant	.029	20.911	.030	20.910
May 21		13.9	770.15	E.		.029	20.901	.028	20.920
						.029	20.921	....	....
May 22	a.m.	8.5	766.00	NE.	Stormy	.031	20.902	.030	20.902
May 22	3h00m p.m.	5.5	764.00	NE. strong		.029	20.902	....	....
May 24		28.0	756.70	W.	Pleasant	.028	20.922	.028	20.920
May 25		19.0	762.85	NW.		.030	20.920	.029	20.920
May 26		....	769.10	NW.	Pleasant	.029	20.921	.030	20.919
May 27		31.2	766.70	S.		.031	20.920	.029	20.920
May 28		14.3	756.70	N.		20.950		....	....
May 29		12.2	752.60	N.		20.950		....	....
June 1		....	762.00	NW.	Pleasant	20.949		....	....
June 2		21.6	764.30	SE.	Cloudy	20.940		....	....
June 3		23.7	760.55	SW.		20.949		....	....
Oct. 18	a.m.	....	....			.031	20.920	....	....
	p.m.	....	....			.032	20.919	....	....
Oct. 19		....	771.45	NW.	Pleasant	.028	20.919	....	....

[1] In all of the analyses of air made in this research, the temperature of the water bath varied from 17° to 21° C. and was usually not far from 19° or 20° C. Subsequent experiments (see p. 97) showed that temperature variations do not materially influence the results.

[2] In this analysis the mercury in the compensation tube was inadvertently brought back to 0 after the carbon dioxide had been absorbed.

west side of the building and those from the east side. In view of these results it was not considered necessary to draw samples from both sides of the building, and only those drawn from the west side were analyzed for the remainder of the research. Aside from certain values which are obviously erroneous, it would appear that the average percentage of oxygen was not far from 20.92, as indicated by this technique and under these conditions. The fluctuations in the percentage of carbon dioxide are those commonly experienced and represent nothing unusual, save that on days when the wind was blowing directly from the thickly settled portion of the city a much higher carbon-dioxide content than at other times

would be expected instead of the constancy indicated. The laboratory is so situated that the wind from the southwest would come from the more residential portion of the city, while the wind from the northeast and east would come from the business and factory part of the city. The power-house of the Harvard Medical School is located exactly north (100 meters) from the laboratory, but aside from this, no large factories or other smoke-producing buildings are nearer than 600 meters.

Errors in first routine.—In October 1909 it was found that if the transfer of gas from pipette *B* to the potassium pyrogallate was continued for some time, there was usually a steady, though slight, increase in the percentage of oxygen, this increase amounting to from 0.001 to 0.002 per cent for each repetition of the routine. Furthermore, the increase continued until the percentage of oxygen had risen from 20.92 to 21 and over, when it could no longer be read accurately, as the graduations extended no farther. It was believed at that time that this increase was due to the distillation of water from the pipette *B* over into the solution of potassium hydroxide. The theory was that the strong alkali had a tension of aqueous vapor considerably less than that of water, and that each time that the air was sent over into the potassium pyrogallate it carried with it a slight amount of moisture; this moisture was retained by the strong alkali until all the water was gradually distilled over.

SECOND ROUTINE, AND RESULTS OBTAINED.

Since it seemed desirable to minimize as much as possible the transfers of air from the measuring pipette into the strong alkali, the first routine was modified somewhat, and a second routine adopted on November 3, 1909. The following changes were made in the method:

The absorption of the carbon dioxide was unchanged, the variation in the routine being chiefly in the determination of oxygen. After the carbon dioxide was absorbed, the gas was sent into the potassium pyrogallate and allowed to remain for 10 minutes. It was then withdrawn and after being sent into the potassium hydroxide was again returned to the potassium pyrogallate and allowed to remain 5 minutes. Then the first reading was taken. This procedure, *i.e.*, once into the potassium hydroxide and a 5-minute sojourn over the potassium pyrogallate, was carried out three times, readings being taken as each routine was concluded.

Results with second routine.—The second routine was followed almost without change from November 3, 1909, until February 15, 1911, samples being taken only on the west side of the laboratory. A sample analysis made on November 4, 1909, is given in table 52. The detailed results for this series of analyses are given in table 53, in which are incorporated, likewise, the temperature of the outdoor air, the barometer, and data regarding the wind and weather, as well as the times at which the analyses were made. These analyses were continued over a period of more than a year, the summer months only being excepted.

TABLE 52.—*Results obtained on sample of outdoor air with second routine, November 4, 1909, 9^h10^m a. m.*

Reading.	Carbon dioxide.	Oxygen.
	p. ct.	*p. ct.*
First	0.035	20.888
Second	0.036	20.909
Third.........	....	20.910

TABLE 53.—*Analyses of outdoor air made at the Nutrition Laboratory. Series 2.*

[All samples were taken from the west side of the laboratory.]

Date.	Time.	Temperature.	Barometer.	Wind.	Weather.	Carbon dioxide.	Oxygen.
1909.		°*C.*	*mm.*			*p. ct.*	*p. ct.*
Nov. 4	9^h10^ma.m.	....	753.25	....	Pleasant	0.036	20.910
Nov 5	3 12 p.m.	4.0	763.60	....	Cold, raw	.029	20.932
						.033	20.949
Nov. 6	10 00 a.m.	....	......	....	....	.035	20.942
						.035	20.940
Nov. 8	9 00 a.m.	8.7	774.95	SW.	Cold, raw	.039	20.920
						.035	20.918
Nov. 10	11 25 a.m.	7.8	779.90	SW.	Pleasant	.034	20.920
						.033	20.923
Nov. 11	9 16 a.m.	11.7	778.00	W.............	....Do.	.035	20.930
						.034	20.930
Nov. 12	8 47 a.m.	17.8	767.05	Very little, if any	....Do.	.030	20.920
						.031	20.931
Nov. 13	8 56 a.m.	11.7	775.55	No wind	Overcast	.035	20.930
						.034	20.927
Nov. 15	8 57 a.m.	11.7	769.90	SW., very little .	....Do.	.035	20.923
						.033	20.922
Nov. 16	8 34 a.m.	6.9	769.90	NW.	Pleasant	.030	20.931
						.030	20.933
Nov. 17	10 34 a.m.	14.9	751.75	Brisk SW.......	Rain	.030	20.921
						.031	20.923
Nov. 18	9 45 a.m.	4.8	......	Brisk NW......	Overcast	.033	20.930
						.034	20.930
Nov. 22	9 14 a.m.	6.8	766.00	SE.	Rain	.033	20.925
						.034	20.920
Nov. 23	8 46 a.m.	17.9	752.50	SW.	Overcast; rained night before, sun out part of time.[1]	.029	20.922
						.031	20.921
Nov. 24	3 31 p.m.	0.0	762.00	Strong NE......	Snow, sleet	.027	20.921
Nov. 29	9 37 a.m.	3.0	764.70	NE.	Stormy	.031	20.923
Dec. 9	10 34 a.m.	— 1	760.00	W.............	Pleasant	.030	20.919
Dec. 21	9 30 a.m.	(1)	760.77	SW.	Pleasant, sunny	.029	20.910
Dec. 22	8 32 a.m.	(1)	756.90	NW.	Sunny, bright ..	.031	20.900
						.032	20.920
Dec. 27	11 16 a.m.	(1)	749.00	W.............	Bright, sunny snow storm day before, about 30 cm. snow.	.028	20.921
	2 37 p.m.	....	749.10	W.............		.031	20.921
Dec. 28	2 52 p.m.	(1)	752.50	Very little, SW.	Pleasant	.029	20.910
						.032	20.923
Dec. 29	10 24 a.m.	— 6	753.00	Light WNW. ..	Foggy	.041	20.903
						.043	20.902
Dec. 30	9 27 a.m.	—12	755.55	NW.	Sunny	.029	20.919
						.031	20.922
Dec. 31	8 57 a.m.	— 8	766.95	W.............	Pleasant	.028	20.911
						.030	20.912
1910							
Jan. 1	8 45 a.m.	— 3	769.65	SW.	Sunny	.031	20.913
						.030	20.913
Jan. 3	8 40 a.m.	1	761.85	SW.	Cloudy	.030	20.921
Jan. 4	9 21 a.m.	—14	775.00	NW	Bright	.029	20.921
Jan. 5	8 50 a.m.	—15	783.30	W.............	Snowing	.032	20.919
Jan. 6	8 58 a.m.	6	761.35	SW.	Rain	.042	20.933
						.035	20.932
Jan. 6	a.m.	6	759.65	SW.	....Do.	.034	......
						.036	
	p.m.					.040	20.920
Jan. 7	8^h43^ma.m.	2	756.00	NW.	Heavy rain	.032	20.930
						.034	20.929
Jan. 7	2 49 p.m.	2	758.10	NW.	Pleasant	.031	20.932
Jan. 8	8 39 a.m.	— 4	778.90	W	....Do.	.031	20.922

[1]Below zero.

TABLE 53.—*Analyses of outdoor air made at the Nutrition Laboratory. Series 2.*—Cont'd.

[All samples were taken from the west side of the laboratory.]

Date.	Time.	Temperature.	Barometer.	Wind.	Weather.	Carbon dioxide.	Oxygen.
1910.		°C.	mm.			p. ct.	p. ct.
Jan. 10	4h00m p.m.	— 2	774.00	NW.	Pleasant	0.029	20.922
Jan. 17	3 49 p.m.	3.0	768.70	E.	Sunny	.031	20.923
Jan. 18	8 54 a.m.	5.0	760.00	SE.	Rain	.033	20.921
Jan. 19	8 35 a.m.	5.0	759.00	NW.	Sunny	.030	20.922
Jan. 24	3 51 p.m.	5.0	765.30	S.W.	Cloudy	.031	20.919
Jan. 25	8 36 a.m.	3.0	764.00	Light NE.	Do.	.030	20.919
Jan. 26	8 50 a.m.	3.0	760.20	W.	Pleasant	.029	20.923
Jan. 27	8 56 a.m.	2.0	748.40	SE.	Cloudy	.031	20.918
Jan. 28	9 00 a.m.	3.0	752.85	SW.	Sunny, bright	.030	20.919
Jan. 29	10 40 a.m.	3.0	743.85	NE.	Rain	.034	20.920
Jan. 31	9 00 a.m.	0.0	762.45	NW.	Cloudy, light snowstorm night before.	.033	20.921
Feb. 1	9 54 a.m.	— 3	762.05	NW.	Pleasant	.029	20.923
Feb. 2	10 05 a.m.	0.0	765.25	NW.	Do.	.028	20.918
Feb. 4	3 49 p.m.	1.0	753.15	NW.	Snow in morning; sunny and pleasant at 3h49m p.m.	.029	20.923
Feb. 5	2 32 p.m.	0.0	752.65	Strong W.	....	.030	20.921
Feb. 7	3 06 p.m.	—10	765.75	Strong NW.	Pleasant	.032	20.919
Feb. 8	2 44 p.m.	4	765.40	SW	Not sunny	.032	20.920
Feb. 11	3 40 p.m.	— 4	778.00	SE.	Cold, raw day, no sun.	.029	20.919
Feb. 12	11 15 a.m.	0.0	747.00	NW.	Snowing and raining, raw day.	.032	20.920
Feb. 17	8 50 a.m.	0.0	766.70	NE.	Cold, raw day, misty.	.031	20.913
						.031	20.912
Mar. 21	2 40 p.m.	10.0	768.75	Light W.	Pleasant, sunny and bright.	.028	20.919
Mar. 24	2 38 p.m.	....	......	....	Do.	.027	20.911
Apr. 1	8 27 a.m.	13.0	767.55	NW.	Do.	.027	20.910
Apr. 4	3 50 p.m.	16.4	765.75	SW.	Cloudy	.028	20.931
Apr. 5	8 10 a.m.	16.0	762.85	No wind	Do.	.030	20.931
	9 12 a.m.	....	......	....	Sunny	.030	20.932
Apr. 7	8 36 a.m.	19.0	751.00	SW.	Slightly overcast, very warm.	.033	20.932
	2 01 p.m.	18.7	750.10	W.	Very cloudy	.030	20.933
Apr. 8	9 12 a.m.	10.2	754.50	NW.	Cloudy	.030	20.940
	10 22 a.m.	....	......	....	....	.029	20.941
Apr. 11	7 59 a.m.	8.3	761.45	NW.	Very pleasant	.029	20.932
Apr. 13	8 19 a.m.	10.2	765.00	SW.	Pleasant, sunny	.030	20.932
Apr. 15	11 48 a.m.	20.2	759.00	W.	Sunny, bright	.029	20.933
Apr. 18	8 26 a.m.	10.9	766.50	No wind	Rained a little	.032	20.939
	9 24 a.m.	....	......	....	....	.030	20.930
Apr. 21	8 42 a.m.	16.0	760.00	SE	Pleasant but not sunny.	.030	20.940
	9 42 a.m.	....	......	....	....	.031	20.942
Apr. 26	2 31 p.m.	15.3	763.90	Light SE	Rainy	.030	20.943
	3 35 p.m.	....	......	....	....	.028	20.921
Apr. 28	10 21 a.m.	9.0	762.00	Strong NW	Pleasant, cool, and windy.	.028	20.933
Apr. 29	8 37 a.m.	12.0	765.90	Light NW	Very pleasant; sunny.	.027	20.921
May 2	8 45 a.m.	10.0	768.40	No wind	Cloudy	.029	20.921
May 3	8 32 a.m.	12.4	764.90	Light SW	Do.	.029	20.940
	9 32 a.m.	....	......	....	....	.029	20.931
May 4	9 07 a.m.	9.8	764.90	NW.	Cloudy	.029	20.932
	10 09 a.m.	....	......	....	....	.031	20.931
May 5	8 33 a.m.	9.2	766.25	Light SW	Cloudy	.030	20.933
	9 31 a.m.	....	......	....	....	.030	20.930
May 6[1]	9 29 a.m.	....	......	....	....	.027	20.960
May 6	12 20 p.m.	15.8	760.00	SW.	Very pleasant; sunny.	.029	20.931
	2 39 p.m.	....	......	....	....	.030	20.922
May 7	9 50 a.m.	20.5	760.00	W.	Pleasant	.033	20.923
May 9	8 42 a.m.	15.8	757.25	SE.	Rainy	.033	20.920
May 10	8 15 a.m.	17.8	755.85	Brisk NW.	Pleasant	.031	20.933
	9 16 a.m.	....	......	....	....	.031	20.922
	10 17 a.m.	....	......	....	....	.030	20.921
May 11	8 28 a.m.	16.8	755.00	SE.	Cloudy	.028	20.922
May 12	3 29 p.m.	14.9	756.50	SE.	Pleasant and sunny.	.029	20.920
May 13	10 53 a.m.	13.3	761.90	SE.	Do.	.033	20.933
	2 35 p.m.	12.9	761.65	SE.	Do.	.030	20.930
May 16	2 36 p.m.	16.5	772.40	No wind	Very pleasant	.029	20.922

[1] Apparatus leaked. All stopcocks were removed and greased.

TABLE 53.—*Analyses of outdoor air made at the Nutrition Laboratory. Series 2*—Cont'd.

[All samples were taken from the west side of the laboratory.]

Date.	Time.	Temperature.	Barometer.	Wind.	Weather.	Carbon dioxide.	Oxygen.
1910.		°C.	mm.			p. ct.	p. ct.
May 17	8h50m a.m.	22.8	770.60	Light SW.	Pleasant, warm and sunny.	0.034	20.922
	9 49 a.m.	....	......	....	....	.033	20.925
	11 01 a.m.	....	......	....	....	.034	20.923
	11 58 a.m.	....	......	....	....	.031	20.921
May 18	2 14 p.m.	15.1	758.55	SE.	Rain	.029	20.923
May 20	2 57 p.m.	23.0	762.80	Light SE.......	Pleasant, sunny	.028	20.911
	3 57 p.m.					.029	20.911
May 21	3 09 p.m.	13.7	761.30	No wind	Rainy, misty ...	.031	20.921
May 23	3 42 p.m.	20.0	763.00	Light SE.......	Cloudy	.032	20.912
	4 42 p.m.	....	......	....	....	.033	20.913
May 24	10 30 a.m.	28.6	756.70	No wind.	Pleasant	.032	20.923
	11 42 a.m.	....	......	....	....	.030	20.902
	3 16 p.m.	....	......	....	....	.030	20.920
May 26	2 14 p.m.	....	......	....	....	.031	20.715
	3 24 p.m.	....	......	....	....	.031	20.743
May 28	1 12 p.m.	18.0	762.40	No wind	Showery	.031	20.911
	2 14 p.m.	....	......	....	....	.032	20.910
May 31	1 19 p.m.	....	......	....	....	.034	20.941
	3 08 p.m.	18.3	747.40	SE.	Cloudy part of time; sunny.	.032	20.942
June 1	1 49 p.m.	17.0	748.20	Strong NW	Not sunny	.029	20.940
	2 52 p.m.	....	......	....	....	.031	20.940
June 2	9 09 a.m.	19.1	751.80	SW	Cloudy	.032	20.920
	10 00 a.m.	....	......	....	....	.030	20.922
June 4	2 24 p.m.	14.7	764.65	SE.	Very pleasant ..	.030	20.930
	3 27 p.m.	....	......	....	....	.028	20.931
June 6	3 17 p.m.	16.4	757.95	NW.	Rainy day, but not raining when analyses were made.	.033	20.930
	4 18 p.m.	....	......	....		.031	20.931
June 7	3 05 p.m.	14.0	......	W.............	Rainy	.031	20.930
	4 10 p.m.	....	......	....	....	.030	20.933
June 8	2 40 p.m.	20.1	761.70	SW.	Pleasant, sunny	.028	20.931
	3 31 p.m.	....	......	....	....	.028	20.921
	4 34 p.m.	....	......	....	....	.028	20.932
	5 27 p.m.	....	......	....	....	.028	20.930
June 9	2 10 p.m.	23.0	765.10	SW.	Pleasant, sunny	.029	20.931
	3 16 p.m.	....	......	....	....	.030	20.933
June 10	9 11 a.m.	12.3	765.25	Strong NE.	Rainy	.028	20.931
	10 14 a.m.	....	......	....	....	.031	20.930
June 11	8 35 a.m.	11.2	766.45	NE.	Rainy	.031	20.933
	9 37 a.m.	....	......	....	....	.030	20.931
June 13	2 28 p.m.	24.2	762.50	SW.	Changeable, cloudy and sunny.	.030	20.941
	3 37 p.m.	....	......	....		.031	20.941
June 14	8 46 a.m.	27.1	763.15	No wind	Pleasant, sunny	.030	20.921
	9 48 a.m.	....	......	....	....	.028	20.921
June 16	8 35 a.m.	19.7	765.45	No wind	Cloudy	.033	20.930
	9 35 a.m.	....	......	....	....	.032	20.921
	10 37 a.m.	....	......	....	....	.032	20.923
June 17	9 05 a.m.	17.8	761.45	NE.	Foggy	.034	20.920
	1 11 p.m.	....	......	....	....	.030	20.921
June 18	2 22 p.m.	23.9	752.90	No wind	Cloudy, showers	.032	20.933
	3 25 p.m.	....	......	....	....	.033	20.932
Jnne 20	8 23 a.m.	....	......	....	....	.030	20.951
	10 25 a.m.	....	......	....	....	.029	20.920
	11 30 a.m.	26.9	759.50	SW.	Sunny, pleasant	.028	20.921
June 21	8 33 a.m.	30.9	758.95	SW.	....Do.	.030	20.921
	9 22 a.m.	....	......	....	....	.028	20.918
June 22	9 03 a.m.	30.1	759.50	W.............	Pleasant; not sunny.	.030	20.930
	10 03 a.m.	....	......	....		.029	20.931
June 23	9 10 a.m.	26.2	755.90	No wind	Cloudy	.030	20.929
	10 11 a.m.	....	......	....	....	.028	20.910
	11 15 a.m.	....	......	....	....	.030	20.931
June 24	9 16 a.m.	24.8	761.00	Light, E........	Sunny, pleasant	.029	20.909
	10 10 a.m.	....	......	....	....	.030	20.933
	11 10 a.m.	....	......	....	....	.031	20.930
June 25	2 02 p.m.	20.5	767.35	Light, SE.......	Pleasant	.031	20.921
	2 54 p.m.	....	......	....	....	.033	20.923
June 27	10 06 a.m.	25.0	759.65	SW.	Pleasant, but not sunny.	.030	20.939
	11 05 a.m.	....	......	....		.030	20.939
June 28	8 55 a.m.	24.9	753.75	NW.	Cloudy	.033	20.933
	10 07 a.m.	....	......	....	....	.031	20.931
June 29	12 31 p.m.	24.3	756.75	NW.	Pleasant and sunny.	.032	20.921
	1 23 p.m.	....	......	....		.031	20.923
June 30	8 38 a.m.	28.0	758.85	W.............	Sunny	.031	20.923
	12 43 p.m.	....	......	....	....	.031	20.923

TABLE 53.—*Analyses of outdoor air made at the Nutrition Laboratory. Series 2*—Cont'd

[All samples were taken from the west side of the laboratory.]

Date.	Time.	Temperature.	Barometer.	Wind.	Weather.	Carbon dioxide.	Oxygen.
1910.		°C.	mm.			p. ct.	p. ct.
July 1	1h35m p.m.	27.8	757.30	Light, SE.	Cloudy	0.029	20.923
	2 34 p.m.	....	......	......	......	.031	20.933
	3 22 p.m.	....	......	......	......	.030	20.934
Oct. 17	3 09 p.m.	....	......	......	......	.030	20.930
	4 08 p.m.	....	......	......	......	.030	20.951
	......	....	......	......	......	.029	....
	......	....	......	......	......	.032	....
Oct. 18	8 53 a.m.	....	......	......	......	.041	20.921
	9 40 a.m.	....	......	......	......	.029	20.942
	11 25 a.m.	....	......	......	......	.027	20.941
	2 36 p.m.	....	......	......	......	.027	20.960
Oct. 19	11 53 a.m.	....	......	......	......	.032	20.900
	3 05 p.m.	....	......	......	......	.029	20.932
	4 16 p.m.	18.7	763.00	SW.	Warm and pleasant.	.029	20.930
Oct. 20	9 00 a.m.	18.1	758.70	No wind	Rain.	.030	20.928
						.029	20.930
						.028	....
						.031	....
						.032	....
Oct. 21	9 45 a.m.	7.7	765.85	NE.	Pleasant	.028	....
	2 37 p.m.	....	......	......	......	.030	20.932
						.030	20.931
						.032	....
						.031	....
						.030	....
Oct. 24	9 18 a.m.	9.9	759.50	NW.	Cool and pleasant.	.029	20.953
	10 25 a.m.	....	......	......		.030	20.941
	11 33 a.m.	....	......	......	......	.030	20.941
	2 34 p.m.	....	......	......	......	.027	20.923
	3 36 p.m.	....	......	......	......	.027	20.924
Oct. 25	8 49 a.m.	9.0	757.50	Light, SW.	......	.032	20.920
	9 45 a.m.	11.8	......	......	......	.030	20.941
	10 44 a.m.	14.1	......	......	......	.032	20.939
Oct. 26	8 56 a.m.	8.6	750.30	Strong NW.	......	.027	20.950
	10 09 a.m.	9.1	......	......	......	.029	20.949
	11 37 a.m.	9.7	......	......	......	.031	20.953
	2 35 p.m.	10.9	752.15	NW.	......	.030	20.943
						.029	....
						.030	....
Oct. 27	2 31 p.m.	9.7	748.50	SW.	......	.028	20.940
	3 23 p.m.	9.5	......	......	......	.030	20.942
						.028	....
						.032	....
						.031	....
Oct. 28	9 07 a.m.	8.5	755.50	SW.	......	.032	20.932
	9 57 a.m.	9.2	......	......	......	.031	20.932
						.029	....
						.031	....
						.030	....
						.033	....
Dec. 2	3 08 p.m.	10.0	757.15	NW.	......	.030	20.941
						.028	20.951
Dec. 6	11 27 a.m.	—7	760.00	NW.	Light snowstorm, first of the winter.	.028	20.940
						.027	20.943
Dec. 7	10 24 a.m.	—2	757.40	Light, NW.	Bright, sunny	.027	20.921
	11 30 a.m.	....	......	......	......	.030	20.940
	12 14 p.m.	....	......	......	......	.028	20.939
Dec. 8	......	....	......	......	......	.028	....
						.031	....
						.031	....
	2 10 p.m.	—0.7	761.75	Light, W.	......	.031	20.941
	3 00 p.m.	....	......	......	......	.028	20.943
Dec. 9	9 07 a.m.	—4.2	765.80	W.	Bright, sunny	.029	20.932
	10 03 a.m.	....	......	......	......	.029	....
	11 37 a.m.	....	......	......	......	.028	20.942
	12 23 p.m.	....	......	......	......	.029	20.943
Dec. 10	2 15 p.m.	—7.3	766.95	Light, W.	Pleasant	.029	20.922
	3 05 p.m.	....	......	......	......	.030	20.940
	4 13 p.m.	....	......	......	......	.030	20.890
Dec. 12	10 13 a.m.	0.0	765.45	......	Bright, sunny	.030	20.943
						.032	20.942
Dec. 13	9 25 a.m.	—1.6	770.00	Light, NW.	Bright, sunny	.030	20.900
	10 13 a.m.	....	......	......	......	.030	20.941
						.030	20.942
Dec. 14	9 41 a.m.	0.2	760.50	SW.	......	.030	20.862
	10 30 a.m.	....	......	......	......	.032	20.941
	11 18 a.m.	....	......	......	......	.031	20.943

TABLE 53.—*Analyses of outdoor air made at the Nutrition Laboratory. Series 2*—Cont'd.

[All samples were taken from the west side of the laboratory.]

Date.	Time.	Temperature.	Barometer.	Wind.	Weather.	Carbon dioxide.	Oxygen.
1910.		°C.	mm.			p. ct.	p. ct.
Dec. 15	9^h43^ma.m.	2.4	748.65	Light, SW.	Not bright and sunny.	0.028	20.938
	10 42 a.m.	....	......	....	....	.030	20.941
Dec. 19	11 04 a.m.	6.6	747.00	Light, W.......	Rained in a.m., but not raining when analyses were made.	.030	20.921
	11 53 a.m.	....	......	....		.032	20.933
	2 20 p.m.	....	......	....		.031	20.962
Dec. 20	9 41 a.m.	....	......	....	....	.032	20.831
	10 37 a.m.	....	......	....	....	.030	....
	11 32 a.m.	....	......	....	....	.031	20.942
	2 04 p.m.	....	......	....	....	.032	20.831
Dec. 22	10 38 a.m.	4.4	770.20	NW.	Bright and sunny	.032	20.932
	11 38 a.m.	....	......	....	....	.032	20.931
Dec. 23	9 42 a.m.	1.9	771.60	Light, SW.	Pleasant	.032	20.923
1911.						.031	20.952
Jan. 18	3 10 p.m.	....	......	....	....		
	4 14 p.m.	....	......	....	....	.031	20.960
Jan. 20	9 31 a.m.	0.0	767.25	Light, W.......	Pleasant and sunny.	.033	20.960
	10 44 a.m.	....	......	....	....	.030	20.950
	11 52 a.m.	....	......	....	....	.029	20.961
	3 29 p.m.	0.0	766.35	Light, SE.	Pleasant	.029	20.961
Jan. 21	9 17 a.m.	6.4	754.60	Brisk SW.......	Cloudy	.030	20.951
Feb. 10	....	0.8	758.00	Light, NW.	Pleasant	.029	20.969
						.027	20.960
						.030	20.961
						.028	20.964
						.028	20.961

As an examination of the results showed frequent marked alterations in oxygen content, numerous experiments were made with a view to changing experimental conditions, an accurate Haldane apparatus being often used. The variations persisted, however, and while the year's work from November 3, 1909, to February 15, 1911, fully substantiated the observations of earlier experimenters, by no stretch of the imagination could a relationship be established between the oxygen percentages and meteorological conditions, nor could any adequate explanation be found as to their cause or causes. The significant fact that there was no corresponding alteration in the carbon-dioxide content—this factor remaining constant under all conditions of wind direction—led us to the belief that the oxygen percentage also approximated constancy, and that the discrepancies appearing in the results might be attributed to errors in either the technique or the apparatus.

CONTROL ANALYSES.

To determine the source of error it was necessary to make duplicate analyses on another apparatus exactly similar in shape; consequently Rudolph Grave, of Stockholm, was commissioned to construct a second apparatus. In the fall of 1910 this apparatus reached Boston, but unfortunately had been utterly demolished in transit. Since it was then too late in the season to secure a third apparatus for the winter's work, the lack of control analyses was a very serious drawback. Finally, a cylinder of compressed air was secured from the compressed-air plant of the Laboratory of Mechanical Engineering at the Massachusetts Institute of

Technology for the purpose of making control analyses of the air in the cylinder. The steel cylinder employed, which had formerly been used for compressed oxygen, was repeatedly exhausted by a vacuum-pump and outdoor air admitted. It was assumed that the inner walls of the cylinder would not absorb oxygen from the air rapidly. It was furthermore assumed that air stored in the large compressed-air chamber of the Institute of Technology would be thoroughly mixed and have a fairly constant composition. Employing precisely the same technical routine, samples of the cylinder air were frequently analyzed as a control on the analyses of the outdoor air. The results of these analyses made between December 3, 1910, and February 9, 1911, are given in table 54.

TABLE 54.—*Analyses made at the Nutrition Laboratory of air confined in a steel cylinder. Series 1.*

Date.	Time.	Carbon dioxide.	Oxygen.	Date.	Time.	Carbon dioxide.	Oxygen.
1910.		*p. ct.*	*p. ct.*	1910.		*p. ct.*	*p. ct.*
Dec. 3	9h34m a.m.	0.033	20.950	Dec. 28	9h38m a.m.	0.032	20.920
Dec. 6	2 35 p.m.	.033	20.942		10 44 a.m.	.032	20.911
	3 37 p.m.	.032	20.943		11 43 a.m.	.033	20.951
Dec. 7	4 48 p.m.	.034	20.941		3 37 p.m.	.032	20.949
Dec. 8	4 03 p.m.	.034	20.943	1911.			
Dec. 9	2 56 p.m.	.032	20.940	Jan. 21	2 32 p.m.	.031	20.951
Dec. 10	10 14 a.m.	.031	20.937		3 43 p.m.	.033	20.950
Dec. 13	12 02 p.m.	.034	20.938	Jan. 23	9 37 a.m.	.032	20.951
Dec. 15	11 52 a.m.	.031	20.922		10 52 a.m.	.033	20.952
Dec. 22	2 31 p.m.	.033	20.922	Jan. 31	10 03 a.m.	.032	20.962
	3 43 p.m.	.033	20.930		11 30 a.m.	.033	20.975
	4 52 p.m.	.034	20.933	Feb. 9	....	.034	20.913
Dec. 23	10 50 a.m.	.034	20.912				
	11 58 a.m.	.032	20.920				
	3 24 p.m.	.032	20.932				

As the simultaneous analyses of outdoor air and cylinder air progressed, it soon became apparent that there was some intimate relation between the fluctuations in oxygen content of the outdoor air and the fluctuations observed in the oxygen content of the cylinder air. Furthermore, while a steady slight decrease in the oxygen percentage of cylinder air might have been expected, as a matter of fact the fluctuations were such as to indicate at times apparent increases. This was conclusive evidence that in spite of all precautions and delicacy of manipulation, the observed fluctuations in the oxygen content of outdoor air might well be due to errors in technique.

THIRD ROUTINE, AND RESULTS OBTAINED.

The fluctuations in the oxygen content of the cylinder air led to the belief than an error was introduced by the distillation of water from the measuring pipette over into the strong alkali. A series of test experiments, which occupied several weeks, almost to the exclusion of regular air-analyses, finally resulted in an alteration in the routine on February 15,

1911. A further change was made at this time which was due to the fact that at the end of an analysis the potassium pyrogallate was in contact with pure nitrogen in the capillary tube inside the chamber, while the reagent in the outer part of the reagent chamber was in contact with air. This was remedied by the attachment of a double bulb to the tube through which the chamber is filled. This double bulb provided a seal, one bulb containing water and the other air. When a sample of air was forced into the pyrogallate vessel, the reagent, rising on the outside of the inner tube, forced the gas above it into the first bulb, thereby expelling the water which it contained into the second bulb.

The modified routine adopted on February 15, 1911, was as follows: After absorbing the carbon dioxide, the air was sent back and forth into the potassium pyrogallate five times, being left there each time 10 seconds. The first reading was then taken. Following this the air was again sent into the potassium pyrogallate for 10 seconds and a second reading taken. This procedure was carried on until the readings were essentially constant. About this time a change was also made in the carbon-dioxide routine. As it appeared unnecessary to make two readings of this factor, the first reading was omitted, although the procedure for transfer of air to and from the potassium-hydroxide pipette was not altered in any way. With this routine, therefore, the air was passed from the measuring pipette into the potassium pyrogallate a maximum of eight times. A sample analysis made with the third routine is given in table 55.

TABLE 55.—*Results obtained on a sample of outdoor air with third routine, February 20, 1911, $4^h\ 25^m$ p. m.*

Reading.	Carbon dioxide.	Oxygen.
	p. ct.	*p. ct.*
First	0.028	20.930
Second	....	20.941
Third	....	20.949
Fourth	....	20.952

This routine was followed for but two days in the regular air-analyses; the few results are given in table 56. During the period from February 16 to March 10 the cylinder air was likewise more or less continually analyzed, the third routine being used. (See table 57.)

TABLE 56.—*Analyses of outdoor air made at the Nutrition Laboratory. Series 3.*

Date.	Time.	Temperature.	Barometer.	Wind.	Weather.	Carbon dioxide.	Oxygen.
1911.	*p.m.*	°*C.*	*mm.*			*p. ct.*	*p. ct.*
Feb. 20	....	—5	755.00	NW.	Snowing all day..	0.028	20.951
	4^h00^m	....	....	....	....	.031	20.950
	4 25	....	....	....	....	.028	20.952
Feb. 21	2 15	—2.8	761.75	W..	Sunny, pleasant..	.028	20.940
	2 40	....	....	....	....	.030	20.941

TABLE 57.—*Analyses made at the Nutrition Laboratory of air confined in a steel cylinder. Series 2.*

Date.	Time.	Temperature of water-bath.	Carbon dioxide.	Oxygen.	Date.	Time.	Temperature of water-bath.	Carbon dioxide.	Oxygen.
1911.		°*C.*	*p. ct.*	*p. ct.*	1911.		°*C.*	*p. ct.*	*p. ct.*
Feb. 16	8h30m a.m.	19.4	0.034	20.951	Feb. 27	10h30m a.m.	17.1	0.033	20.929
		19.6	.034	20.950		11 00 a.m.	17.0	.032	20.933
	11 15 a.m.	19.6	.035	20.941		12 00 noon	26.0	.032	20.943
	2 15 p.m.	19.4	.036	20.951		3 30 p.m.	24.8	.030	20.932
		19.7	.035	20.953			25.2	.029	20.939
Feb. 18	2 15 p.m.	20.4	.033	20.952			25.7	.030	20.931
		20.6	.033	20.949	Feb. 28	8 45 a.m.	16.7	.033	20.910
Feb. 20	....	19.6	.035	20.938		9 25 a.m.	16.8	.034	20.930
	5 00 p.m.	20.1	.033	20.943		9 45 a.m.	16.9	.033	20.930
Feb. 21	....	17.5	.033	20.931		10 15 a.m.	16.8	.035	20.931
		17.3	.033	20.932		11 05 a.m.	26.0	.032	20.922
		17.9	.034	20.935		11 25 a.m.	26.3	.028	20.942
		25.9	.032	20.942		11 50 a.m.	25.9	.030	20.941
	11 45 a.m.	25.3	.033	20.941	Mar. 1	2 35 p.m.	16.8	.033	20.921
		25.3	.032	20.950		3 10 p.m.	16.8	.034	20.921
		25.4	.031	20.950		3 35 p.m.	16.5	.034	20.920
	3 45 p.m.	17.2	.033	20.900		4 00 p.m.	17.0	.033	20.920
	4 20 p.m.	17.3	.033	20.933			17.2	.033	20.921
	5 00 p.m.	17.3	.035	20.931	Mar. 2	4 00 p.m.	16.4	.033	20.882
Feb. 22	8 25 a.m.	17.4	.034	20.927			16.5	.035	20.911
	9 30 a.m.	26.1	.035	20.920			16.7	.031	20.901
	9 55 a.m.	26.1	.032	20.939	Mar. 3	8 30 a.m.	18.1	.034	20.932
	10 50 a.m.	25.3	.035	20.930		9 00 a.m.	18.1	.033	20.923
	11 25 a.m.	25.5	.034	20.941		9 30 a.m.	18.1	.033	20.929
Feb. 23	8 30 a.m.	17.7	.034	20.929		10 00 a.m.	18.1	.033	....
	9 00 a.m.	16.8	.035	20.931		10 30 a.m.	18.0	.034	20.930
	9 35 a.m.	17.2	.033	20.930		11 00 a.m.	17.8	.034	20.931
	10 30 a.m.	26.2	.032	20.922	Mar. 4	2 20 p.m.	19.6	.035	20.929
	10 55 a.m.	26.0	.029	20.949		2 45 p.m.	19.7	.034	20.930
	11 30 a.m.	25.9	.031	20.941		3 15 p.m.	19.8	.034	20.921
	12 00 noon	25.8	.030	20.939	Mar. 6	....	18.5	.034	20.920
Feb. 24	8 25 a.m.	16.6	.033	20.920			18.7	.031	20.940
	8 50 a.m.	16.3	.034	20.932			18.6	.034	20.919
	9 20 a.m.	16.1	.034	20.921	Mar. 7	8 40 a.m.	18.5	.032	20.910
	10 20 a.m.	26.4	.033	20.938			18.5	.034	20.920
	10 50 a.m.	26.1	.032	20.930		9 25 a.m.	18.6	.034	20.912
	11 15 a.m.	26.0	.031	20.930		3 15 p.m.	18.8	.033	20.912
Feb. 25	2 30 p.m.	17.2	.033	20.921			18.4	.033	20.910
	3 00 p.m.	17.3	.033	20.920			18.5	.034	....
Feb. 27	....	16.4	.032	20.930			18.6	.031	20.930
	9 50 a.m.	16.6	.033	20.941	Mar. 10	8 40 a.m.	17.9	.033	20.921

EFFECT ON OXYGEN ABSORPTION OF HIGH AND LOW TEMPERATURES.

An examination of the results in table 57 shows an approach to constancy, but the variations are still too wide to be permitted in this study. During this period it is seen that the temperature of the water-bath had a wide variation, ranging from 16.1° C. to 32.2° C. Owing to the fact that a number of investigators with whom I had conferred in a recent European tour had suggested that the absorption of oxygen might be profoundly affected by changes in temperature, the wide range was artificially produced for the special purpose of studying this particular point. From the data in table 57 the volumes for the various temperatures have been rearranged so as to give the average results at approximately an average temperature. These results have been incorporated in table 58. An apparently constantly decreasing percentage of carbon dioxide is not considered here, since subsequent experiments show that the decrease is not an inevitable accompaniment of increased temperature. The oxygen determinations show a difference of 0.01 per cent between the value at 17.1° C. and that at 25.8° C., but an insignificant difference between the

value at 25.8° C. and that 6 degrees higher. The low value at 17.1° C. may in part be attributed to the well-known slow absorbing action of potassium pyrogallate at low temperatures. From these results we may safely conclude that temperature changes in the reagent are without appreciable effect upon the absorption of oxygen within the limits mentioned, *i.e.*, between 17.1° C. and 31.8° C.

TABLE 58.—*Analyses made at the Nutrition Laboratory of air confined in a steel cylinder, using high and low temperatures of water-bath.*

Temperature of water-bath.	Carbon dioxide.	Oxygen.	Temperature of water-bath.	Carbon dioxide.	Oxygen.	Temperature of water-bath.	Carbon dioxide.	Oxygen.
°C.	p. ct.	p. ct.	°C.	p. ct.	p. ct.	°C.	p. ct.	p. ct.
17.8	0.033	20.931	25.9	0.032	20.942	32.2	0.032	20.940
17.3	.033	20.932	25.3	.033	20.941	31.3	.030	20.932
17.9	.034	20.935	25.3	.032	20.950	31.4	.029	20.933
17.2	.033	20.900	25.4	.031	20.950	31.8	.030	20.943
17.3	.033	20.933	26.1	.035	20.920	31.9	.031	20.941
17.2	.035	20.931	26.1	.032	20.939	31.9	.028	20.949
17.4	.034	20.927	25.3	.035	20.930	31.9	.030	20.949
17.7	.034	20.929	25.5	.034	20.941	31.7	.031	20.941
16.8	.035	20.931	26.1	.032	20.922			
17.2	.033	20.930	26.0	.029	20.949			
16.6	.033	20.920	25.9	.031	20.941			
16.3	.034	20.932	25.8	.030	20.939			
16.1	.034	20.921	26.4	.033	20.938			
			26.1	.032	20.930			
			26.0	.031	20.930			
Avg. 17.1	.033	20.927	25.8	.032	20.937	31.8	.030	20.941

Errors in the third routine.—Two fundamental alterations in routine were introduced at this time. Miss Johnson called my attention to the fact that after absorbing the oxygen, to connect the pipette *B* with the manometer and then subsequently to send the air into the potassium pyrogallate was illogical for the following reason:

When the stop-cock *a* is turned so as to communicate the gas in *B* with the manometer, there is in *B* only nitrogen. On the other hand, in the capillary between the stop-cocks *a* and *d* there is air. During the short time required to set the manometer and take the reading, there is unquestionably a slight diffusion of air from the capillary into the chamber *B*. Subsequently, when this gas is passed into the potassium pyrogallate, there is a further contraction in volume which results in a considerable increase in the apparent percentage of oxygen. Probably the increased percentages found when the gas was repeatedly passed into the reagents were due to this fact rather than to the distillation of water. It was apparent, therefore, that before connection with the manometer is made, the gas must be sufficiently in contact with the potassium pyrogallate to absorb all of the oxygen, and that no subsequent passage of the gas in *A* into the reagent should be made. Accordingly the routine was so changed as to secure these conditions.

Shortly prior to this, it was believed that when the mercury was raised and lowered in pipette *B*, the amount of water adhering to the walls of the lower bulb and graduated portion would vary, and that these differences might play a very important rôle in determining the percentage of oxygen. Experiments were accordingly made to find the oxygen percentage in air more or less dry, but these were unsuccessful. Finally, it was decided that if an excess of water was present in the pipette the same relative amount of water would probably adhere to the glass walls each time.

A large number of experiments were made to determine the amount of water which should be added to obtain a clear meniscus for reading and to insure constancy in the amount of water in the pipette. At first minute quantities of water were used, the attempt being made to secure only enough to saturate the gas with moisture. It was assumed that when the mercury was lowered the liquid water would adhere to the inside of the upper bulb, so that only the mercury would enter the constricted portion of the pipette and the lower bulb, and that no liquid water would be present. Under these conditions, however, it was found very difficult to set the meniscus, and the following routine was finally decided on:

FOURTH ROUTINE, AND RESULTS OBTAINED.

Outline of fourth routine.—The nitrogen resulting from the previous analysis was stored temporarily in the potassium-pyrogallate pipette, the capillary tube leading to the carbon-dioxide absorption chamber *C* also being filled with nitrogen. The stop-cock *a* was next removed and the mercury in the pipette *B* raised up through the capillary to the stop-cock. Water was then added and the mercury simultaneously lowered until there was a layer of 17 mm. of water above it in the capillary tube. The stop-cock *a* was again put in place, the nitrogen withdrawn from the pyrogallate reservoir, and the sample taken and analyzed as usual.

Results with fourth routine.—The analyses made with this routine were continued from March 28 to April 10, 1911. The results are given in table 59. When these results are compared with those of earlier experiments, it will be noted that notwithstanding the differences in temperature, barometer, direction of the wind, and other conditions, the oxygen determinations show a striking uniformity, the variations previously found practically disappearing.

This new routine was also used for the analyses of cylinder air, which provided an excellent control of the apparatus and method. The results for the period between March 28 and April 14, 1911, are given in table 60. Here again it is seen that variations in the oxygen percentage are rare, and as used the method may be assumed to give constant results.

TABLE 59.—*Analyses of outdoor air made at the Nutrition Laboratory. Series 4.*

Date.	Time.	Temperature.	Barometer.	Wind.	Weather.	Carbon dioxide.	Oxygen.
		°C.	mm.			p. ct.	p. ct.
Mar. 28	11h30m a.m.	....	748.40	....	Pleasant	0.034	20.938
	12 00 noon	....	....	....	....	.031	20.940
	2 25 p.m.	....	....	....	....	.033	20.949
	3 27 p.m.	....	....	....	....	.030	20.942
Mar. 29	10 01 a.m.	7.6	753.85	Light, SW .	Sunny, pleasant ...	.032	20.921
	10 31 a.m.	....	....	....	....	.030	20.928
	10 59 a.m.	....	....	....	....	.030	20.938
	11 28 a.m.	....	....	....	....	.030	20.932
	11 56 a.m.	....	....	....	....	.029	20.935
	2 45 p.m.	7.4	751.90	N.	Sunny at times, then dark again.	.031	20.939
						.030	20.939
Mar. 30	10 21 a.m.	9.6	739.40	Brisk NW..	....	.029	20.941
	10 52 a.m.	....	....	....	Sunny, pleasant....	.027	20.938
Mar. 31	8 28 a.m.	5.7	746.10	Brisk W ...	Sunny at times, then dark.	.030	20.938
	8 58 a.m.	....	....	....		.029	20.938
Apr. 1	9 00 a.m.	4.5	757.45	W.........	Sunny, pleasant ...	.029	20.938
	9 28 a.m.	....	....	....	....	.030	20.932
	9 57 a.m.	....	....	....	....	.028	20.939
Apr. 3	10 27 a.m.	2.6	770.85	W.........	Sunny, pleasant ...	.031	20.925
	11 05 a.m.	....	....	....	....	.027	20.931
	11 37 a.m.	....	....	....	....	.029	20.938
	12 10 p.m.	....	....	....	....	.031	20.940
Apr. 4	8 26 a.m.	4.2	777.70	Light, E....	Sunny, pleasant....	,031	20.930
	8 54 a.m.	....	....	....	....	.031	20.932
	2 24 p.m.	2.1	775.40	Light, SE .	Damp, raw; no sun	.031	20.931
	2 53 p.m.	....	....	....	....	.031	20.933
Apr. 5	10 06 a.m.	3.6	759.50	Light, SW.	Snow and sleet last night.	.032	20.923
	10 35 a.m.	....	....	....		.032	20.929
	11 06 a.m.	....	....	....	Snow on ground; raining.	.032	20.928
Apr. 6	8 43 a.m.	14.0	757.00	Light, W...	Pleasant, sunny ...	.033	20.940
	9 13 a.m.	....	....	....	....	.031	20.939
A pr 7	9 06 a.m.	16.8	754.40	SW	Sunny, bright......	.032	20.937
	9 32 a.m.	....	....	....	....	.029	20.930
	10 01 a.m.	....	....	....	....	.030	20.931
Apr. 8	11 21 a.m.	8.0	769.00	SW., moderate.	Bright, sunny	.028	20.930
	11 49 a.m.	....	....	....	....	.028	20.938
	12 19 p.m.	....	....	....	....	.030	20.938
Apr. 10	8 45 a.m.	8.6	772.70	Light, W...	Sunny, pleasant ...	.031	20.928
	9 15 a.m.	....	....	....	....	.030	20.935
	9 45 a.m.	....	....	....	....	.031	20.932
	3 32 p.m.	9.9	772.40	Light, W...	Sunny, pleasant ...	.029	20.930

TABLE 60.—*Analyses made at the Nutrition Laboratory of air confined in a steel cylinder. Series 3.*

Date.	Time.	Carbon dioxide.	Oxygen.	Date.	Time.	Carbon dioxide.	Oxygen.
1911.		p. ct.	p. ct.	1911.		p. ct.	p. ct.
Mar. 28	9h06m a.m.	0.038	20.930	Apr. 11	4h04m p.m.	0.034	20.919
	9 25 a.m.	.034	20.922		4 36 p.m.	.033	20.912
	10 00 a.m.	.033	20.921	Apr. 12	8 20 a.m.	.035	20.917
	10 30 a.m.	.032	20.921		9 06 a.m.	.033	20.913
	4 22 p.m.	.036	20.922		9 40 a.m.	.033	20.918
Mar. 29	8 30 a.m.	.034	20.919		10 48 a.m.	.036	20.913
	9 20 a.m.	.036	20.920		11 25 a.m.	.032	20.915
	12 10 p.m.	.034	20.919		11 57 a.m.	.033	20.915
	3 48 p.m.	.032	20.918		2 38 p.m.	.034	20.920
Mar. 30	8 35 a.m.	.031	20.910		3 13 p.m.	.034	20.912
	9 17 a.m.	.033	20.918		3 53 p.m.	.031	20.918
	9 47 a.m.	.032	20.919	Apr. 13	8 34 a.m.	.036	20.910
	11 10 p.m.	.034	20.920		9 05 a.m.	.036	20.909
Apr. 5	11 43 a.m.	.033	20.920		9 36 a.m.	.034	20.912
Apr. 6	9 57 a.m.	.033	20.919		10 13 a.m.	.036	20.911
Apr. 7	10 29 a.m.	.031	20.917		11 06 a.m.	.034	20.914
	10 57 a.m.	.033	20.911		11 52 a.m.	.035	20.920
Apr. 10	2 54 p.m.	.035	20.912	Apr. 14	8 56 a.m.	.034	20.903
Apr. 11	9 12 a.m.	.033	20.910		9 27 a.m.	.033	20.904
	9 46 a.m.	.033	20.912		10 02 a.m.	.035	20.913
	3 00 p.m.	.035	20.916		10 35 a.m.	.033	20.910
	3 32 p.m.	.034	20.910		11 16 a.m.	.034	20.912

FIFTH ROUTINE, AND RESULTS OBTAINED.

A final change in the routine was made on April 15, 1911. When using a layer of 17 mm. of water in the capillary tube of pipette *B* it was found that variations in the percentage of oxygen in cylinder air were occasionally experienced which were somewhat greater than it was believed the method should allow. A few preliminary tests indicated that more uniform conditions of moisture in the pipette could be obtained by another procedure, and the following routine has since been adopted:

Outline of fifth routine.—The nitrogen remaining from the earlier analysis having been stored over the potassium hydroxide and potassium pyrogallate, the stop-cock *b* is closed and the plug of stop-cock *a* is withdrawn. The pipette *B* is first completely filled with mercury. Water is then introduced through the open stop-cock *a*, exactly as in the preceding routine, and the mercury in pipette *B* simultaneously lowered, thus drawing the water down through the capillary tube into the pipette. This is continued until the mercury is lowered to the zero-point, and several times the amount of water previously used has been introduced. The whole interior of the pipette is thus thoroughly drenched with water. The mercury is again raised, expelling all of the visible water, so that none remains above the mercury, filter paper inserted in the cock opening being used to remove the water. The stop-cock is then inserted, and the nitrogen is drawn from the two absorption pipettes, the levels of the potassium hydroxide and potassium pyrogallate are set, and the analysis proceeds in the usual way, *i.e.*, the carbon dioxide is absorbed by sending the gas twice into the potassium hydroxide, taking but one final reading; the air is next passed into the potassium pyrogallate for 5 minutes, then withdrawn, and passed into the potassium hydroxide once. It is again drawn back and passed into the potassium pyrogallate for 1 minute, then into the potassium pyrogallate for 5 minutes, and into the potassium hydroxide once. The level of the latter reagent is now set. The gas is finally sent into the potassium pyrogallate for 1 minute, the level is set, and the reading taken. All the capillaries now being filled with nitrogen as at the beginning of the analysis, the contraction in volume represents the percentage of carbon dioxide in the air and the percentage of oxygen in carbon-dioxide-free air. This routine, which has been followed without any variation since April 15, 1911, has proved eminently satisfactory.

Results with fifth routine.—The results of the analyses of uncontaminated outdoor air between April 15, 1911, and January 9, 1912, as given in table 61, are conclusive in showing that no fluctuation of any magnitude occurs in the percentage of oxygen in air. Certain values lower than the average may be almost invariably attributed to the fact that after new potassium pyrogallate is placed in the reagent vessel the first analysis is inclined to show a somewhat low percentage of oxygen. When it is considered that all of the determinations, with the single exception of a short series from September 15 to 25, 1911, are reported, the accidental variations are indeed inconsiderable.

TABLE 61.—*Analyses of outdoor air made at the Nutrition Laboratory. Series 5.*

Date.	Time.	Temperature.	Barometer.	Wind.	Weather.	Carbon dioxide.	Oxygen.
1911.		°C.	mm.			p. ct.	p. ct.
Apr. 15	4h25m p.m.	11.8	757.15	Light, SW.	Cloudy, dark, a. m.; bright, sunny at 4 p.m	0.031	20.941
	4 56 p.m.	....	....	....		.031	20.939
Apr. 17	11 45 a.m.	10.4	758.50	Light, SW.	Sunny, pleasant....	.030	20.938
	3 00 p.m.	10.0	757.30	Light, SW.	....Do....	.030	20.940
	3 28 p.m.	....	....	....	....	.030	20.940
Apr. 22	4 12 p.m.	3.6	766.05	Brisk NE...	Cold, raw	.031	20.937
	4 48 p.m.	....	....	....	....	.029	20.931
Apr. 24	11 47 a.m.	12.2	765.15	Light, SE	Sunny, pleasant....	.032	20.938
	12 21 p.m.	....	....	....	....	.033	20.940
Apr. 25	11 15 a.m.	12.4	766.80	Light, SE.	Sunny, pleasant....	.032	20.943
	11 55 a.m.	....	....	....	....	.031	20.942
Apr. 26	8 55 a.m.	18.1	772.80	Light, S.	Sunny, pleasant....	.030	20.932
	9 33 a.m.	....	....	....	....	.031	20.940
	10 13 a.m.	....	....	....	....	.031	20.942
Apr. 27	8 45 a.m.	22.9	774.70	N.	Sunny, pleasant....	.031	20.941
	9 25 a.m.	....	....	....	....	.030	20.939
Apr. 28	8 58 a.m.	24.5	770.40	N.	Sunny, pleasant....	.031	20.930
	9 34 a.m.	....	....	....	....	.030	20.939
	10 05 a.m.	....	....	....	....	.031	20.937
Apr. 28	3 09 p.m.	24.5	766.25	N.	Sunny, pleasant....	.030	20.930
	3 54 p.m.	....	....	....	....	.031	20.939
	4 31 p.m.	....	....	....	....	.031	20.938
Apr. 29	8 31 a.m.	25.0	763.90	N.	Sunny, pleasant....	.030	20.929
	9 12 a.m.	....	....	....	....	.033	20.938
	9 57 a.m.	....	....	....	....	.032	20.932
	2 25 p.m.	25.6	761.15	Light, S.	Sunny, pleasant....	.029	20.931
	2 58 p.m.	....	....	....	....	.032	20.937
	3 43 p.m.	....	....	....	....	.032	20.939
May 1	8 45 a.m.	16.7	756.55	Light, SW.	Rain night before, clear but not sunny at time of sampling.	.030	20.938
	9 22 a.m.	....	....	....		.031	20.941
	2 53 p.m.	22.0	752.85	Light, S.	Bright, sunny	.028	20.939
	3 36 p.m.	....	....	....	....	.030	20.941
May 2	8 26 a.m.	19.7	750.90	Brisk W ...	Sunny at times, then dark.	.031	20.943
	9 14 a.m.	....	....	....		.028	20.931
	9 53 a.m.	....	....	....	....	.029	20.933
	11 26 a.m.	....	....	....	....	.028	20.939
	12 10 p.m.	....	....	....	....	.031	20.942
	2 32 p.m.	13.5	752.35	Brisk W ...	Sunny, bright	.030	20.939
	3 03 p.m.	....	....	....	....	.029	20.938
May 3	10 37 a.m.	9.1	760.00	Brisk W.	Cloudy, cold	.029	20.921
	11 13 a.m.	....	....	....	....	.030	20.929
	11 54 a.m.	....	....	....	....	.028	20.932
May 5	8 54 a.m.	....	768.70	Light, SW.	Sunny, bright	.030	20.933
	9 43 a.m.	....	....	....	....	.030	20.940
	10 29 a.m.	....	....	....	....	.031	20.937
	2 33 p.m.	18.6	767.10	N.	Sunny, pleasant....	.031	20.937
	3 04 p.m.	....	....	....	....	.031	20.938
May 6	8 45 a.m.	20.4	770.10	Light, SW	Sunny, bright	.031	20.928
	9 24 a.m.	....	....	....	....	.031	20.932
	10 09 a.m.	....	....	....	....	.029	20.943
	10 48 a.m.	....	....	....	....	.029	20.930
May 19	9 23 a.m.	20.1	762.40	SE.	Cloudy	.031	20.930
	10 09 a.m.	....	....	....	....	.032	20.938
	10 47 a.m.	....	....	....	....	.032	20.931
	11 49 a.m.	21.4	762.65	SE.	Sunny	.032	20.938
	12 27 p.m.	....	....	....	....	.031	20.940
	1 04 p.m.	....	....	....	....	.032	20.940
	3 44 p.m.	14.1	763.60	E.	Cloudy, cold, raw ..	.032	20.942
May 20	8 34 a.m.	19.3	766.10	Brisk SE. ..	Sunny, smoky	.033	20.929
	9 33 a.m.	....	....	....	....	.033	20.929
	10 14 a.m.	....	....	....	....	.033	20.931
May 22	9 15 a.m.	33.2	763.25	Light, SE.	Sunny, bright	.031	20.929
	9 57 a.m.	....	....	....	....	.030	20.940
	11 20 a.m.	....	....	....	....	.031	20.940
	11 55 a.m.	....	....	....	....	.032	20.943
May 23	8 40 a.m.	13.9	769.40	Strong NE	Cold, raw, not sunny.	.029	20.944
	9 18 a.m.	....	....	....		.028	20.942
	9 59 a.m.	....	....	....	....	.031	20.942
	3 52 p.m.	12.2	769.45	Brisk NE ..	Cold, not sunny ...	.029	20.947
May 24	8 28 a.m.	12.9	766.40	Light E. ...	Dark; fog or smoke .	.028	20.940
	10 02 a.m.	....	....	....	....	.030	20.938
May 25	10 09 a.m.	19.2	760.50	Brisk SE. ..	Sunny	.029	20.941
	10 48 a.m.	....	....	....	....	.030	20.938
	12 47 p.m.	....	....	....	....	.029	20.940
May 26	8 55 a.m.	17.5	764.00	Light SW. .	Cloudy, no rain	.029	20.941
	10 18 a.m.	....	....	....	....	.030	20.939
June 1	2 41 p.m.	21.6	753.20	Brisk W ..	Sunny, pleasant....	.028	20.948
	3 19 p.m.	....	....	....	....	.028	20.942

TABLE 61.—*Analyses of outdoor air made at the Nutrition Laboratory. Series 5*—Cont'd.

Date.	Time.	Temperature.	Barometer.	Wind.	Weather.	Carbon dioxide.	Oxygen.
1911.		°*C.*	*mm.*			*p. ct.*	*p. ct.*
	3h59m p.m.	....	....	....	....	0.029	20.937
June 2	8 34 a.m.	24.7	759.40	Brisk W....	Sunny, pleasant....	.029	20.943
	9 14 a.m.	....	....	....	....	.028	20.939
	9 59 a.m.	....	....	....	....	.030	20.940
June 3	8 59 a.m.	23.4	765.55	Light SW ..	Clear; no sun	.029	20.937
	9 42 a.m.	....	....	....	....	.028	20.938
June 5	11 55 a.m.	15.4	767.00	Brisk SE...	Not sunny	.028	20.939
	2 52 p.m.	....	....	....	....	.027	20.939
	3 33 p.m.	....	....	....	....	.030	20.942
June 6	10 31 a.m.	12.5	766.20	Brisk NE ..	Rains	.028	20.942
	11 13 a.m.	....	....	....	....	.029	20.941
	12 19 p.m.	....	....	....	....	.030	20.941
	3 08 p.m.	....	....	....	....	.030	20.949
	3 47 p.m.	....	....	....	....	.029	20.943
June 7	12 32 p.m.	16.4	768.45	Light E. ...	Clear, bright	.028	20.943
	2 18 p.m.	....	....	....	....	.029	20.949
	2 58 p.m.	....	....	....	....	.029	20.942
June 8	8 30 a.m.	20.5	767.05	Brisk NE...	Sunny, pleasant....	.027	20.939
	9 15 a.m.	....	....	....	....	.029	20.943
	9 55 a.m.	....	....	....	....	.029	20.942
June 9	11 50 a.m.	25.3	760.50	Light E....	Sunny, pleasant....	.028	20.939
	3 17 p.m.	....	....	....	....	.029	20.942
	3 57 p.m.	....	....	....	....	.029	20.943
June 10	10 45 a.m.	23.7	757.30	Light NE ..	Warm, sunny early; dark when samples were taken.	.027	20.949
	11 55 a.m.	....	....	....		.029	20.928
	2 34 p.m.	....	....	....		.029	20.934
	3 11 p.m.	....	....	....		.029	20.939
	3 51 p.m.	....	....	....		.031	20.938
	4 27 p.m.	....	....	....		.027	20.941
June 12	9 10 a.m.	....	....	....	....	.046	20.940
	9 48 a.m.	....	....	....	....	.032	20.929
	10 35 a.m.	....	....	....	....	.030	20.939
	2 40 p.m.	....	....	....	....	.027	20.958
	3 19 p.m.	....	....	....	....	.029	20.952
June 13	8 34 a.m.	12.7	755.35	Light SE...	Rained a. m.; no thunder.	.029	20.939
	9 18 a.m.	....	....	....		.028	20.941
	10 27 a.m.	....	....	....	....	.033	....
	12 16 p.m.	....	....	....	....	.029	20.948
	2 43 p.m.	....	....	....	Light thunder; heavy rainfall.	.028	20.930
	3 30 p.m.	....	....	....		.031	20.929
	4 31 p.m.	....	....	....	....	.037	20.936
Sept. 26[1]	8 56 a.m.	15.7	764.00	Light NW..	Not raining; rained early; heavy thunder-storm night before.	.031	20.935
	9 34 a.m.	....	....	....		.029	20.940
Sept. 27	8 35 a.m.	17.0	766.55	Light SW. .	Dull, dark	.032	20.893
	9 09 a.m.	....	....	....	....	.032	20.930
	9 45 a.m.	....	....	....	....	.032	20.930
	4 12 p.m.	....	....	....	....	.029	20.942
Sept. 28	9 07 a.m.	12.4	764.55	Brisk NW..	Sunny, pleasant....	.030	20.949
	9 44 a.m.	....	....	....	....	.032	20.941
	10 19 a.m.	....	....	....	....	.030	20.947
Sept. 29	8 46 a.m.	....	....	....	....	.033	20.932
	9 27 a.m.	....	....	....	....	.039	20.932
						.033	....
						.031	....
	10 33 a.m.	....	....	....	....	.032	20.941
	11 53 a.m.	....	....	....	....	.031	20.938
Sept. 30	8 51 a.m.	11.8	762.90	Brisk NW..	Sunny, pleasant....	.030	20.942
	9 30 a.m.	....	....	....	....	.031	20.942
Oct. 2	9 13 a.m.	8.9	758.30	Mod. NW..	Rains............	.032	20.943
	9 50 a.m.	....	....	....	....	.031	20.940
Oct. 3	8 48 a.m.	11.3	770.30	Light W ...	Sunny, pleasant....	.028	20.939
	9 27 a.m.	....	....	....	....	.031	20.940
Oct. 4	8 45 a.m.	13.6	760.00	Brisk SE ..	Dark; rainy day ...	.031	20.938
	10 12 a.m.	....	....	....	....	.033	20.928
	10 51 a.m.	....	....	....	....	.035	20.931
	3 26 p.m.	18.4	752.00	Brisk SW...	Showers; not raining now.	.030	20.941
Oct. 5	12 03 p.m.	....	758.75	Brisk NW..	....	.027	20.934
	12 37 p.m.	....	....	....	....	.029	20.941
Oct. 6	8 34 a.m.	13.6	762.65	Light SW ..	Pleasant	.028	20.940
Oct. 7	2 30 p.m.	8.0	762.00	Mod. NW..	Rain; cold; raw....	.028	20.941
Oct. 11	9 10 a.m.	....	....	....	....	.031	20.925
Oct. 12	10 00 a.m.	20.4	753.60	Light W ...	Pleasant	.027	20.929

[1] Active experimenting began again on September 15, 1911, but the results for the first few days were obviously influenced by some as yet undetermined factor and are not here included. *These are the only omissions in the entire series.*

TABLE 61.—*Analyses of outdoor air made at the Nutrition Laboratory. Series 5*—Cont'd.

Date.	Time.	Temperature.	Barometer.	Wind.	Weather.	Carbon dioxide.	Oxygen.
1911.		°C.	mm.			p. ct.	p. ct.
Oct. 12	3h32mp.m.	....	....	....	....	0.029	20.937
Oct. 13	8 48 a.m.	9.0	761.70	Brisk W ...	Beautiful clear day .	.030	20.941
Oct. 17	9 28 a,m,	11.5	768.10	Strong NE	Cloudy, fine mist ..	.030	20.938
Oct. 18	4 32 p.m	12.5	762.80	Brisk SE ..	Rained all day	.031	20.939
Oct. 26	9 55 a.m.	14.7	767.00	SW	Sunny, pleasant....	.030	20.930
	10 33 a.m.	....	....	....	....	.031	20.936
	11 05 a.m.	....	....	....	....	.030	20.939
Nov. 1	3 14 p.m.	7.5	763.15	Light NW..	Cold, raw	.032	20.931
	3 23 p.m.	....	....	....	....	.031	20.937
Nov. 13	9 39 a.m.	1.4	764.30	Brisk NW..	Sunny, pleasant....	.029	20.930
	10 14 a.m.	....	....	....	....	.028	20.941
	10 51 a.m.	....	....	....	....	.028	20.939
Nov. 14	9 12 a.m.	.8	773.20	Light W ...	Sunny, bright	.021	20.938
	10 04 a.m.	....	....	....	....	.029	20.938
	10 38 a.m.	....	....	....	....	.029	20.940
Nov. 15	8 55 a.m.	5.8	749.15	N	Bright, sunny; light fall of snow evening before, followed by heavy rain.	.030	20.935
	9 44 a.m.	....	....	....		.028	20.939
	2 25 p.m.	....	....	....		.026	20.940
	2 59 p.m.	....	....	....		.029	20.942
	3 39 p.m.	....	....	....		.029	20.939
	4 23 p.m.	4.6	....	Light W ...	Pleasant	.027	20.941
Nov. 17	12 12 p.m.	4.9	764.70	Brisk W ...	Cold, clear	.026	20.941
Nov. 20	2 13 p.m.	4.7	761.20	Light W ...	Cold, raw	.028	20.940
	2 46 p.m.	....	....	....	....	.030	20.934
	3 31 p.m.	....	....	....	....	.029	20.939
Dec. 4	9 49 a.m.	—3.0	765.15	Light NE .	Cold, raw; no sun .	.029	20.940
	10 28 a.m.	....	....	....	....	.030	20.940
	11 04 a.m.	....	....	....	....	.028	20.939
	11 39 a.m.	....	....	....	....	.030	20.939
	2 21 p.m.	—2.5	765.30	Light N ...	Cold, raw	.031	20.941
	....	....	....	....	....	.031	20.939
Dec. 9	12 01 a.m.	....	773.15	....	Quite foggy	.034	20.931
	....	....	....	....	....	.035	20.931
	3 00 a.m.	....	773.00	....	Not very foggy.....	.033	20.932
	....	....	....	....	....	.034	20.935
	10 12 a.m.	7.8	770.30	SW	Dark; light misty rain.	.030	20.938
	3 57 p.m.	....	....	....		.031	20.940
Dec. 12	12 01 a.m.	....	....	....	Fair	.029	20.939
	3 00 a.m.	....	....	....	Fair	.029	20.941
	8 47 a.m.	16.0	766.55	Light SW ..	Sunny, pleasant....	.028	20.939
Dec. 13	12 01 a.m.	....	....	....	Cloudy	.028	20.938
	3 00 a.m.	....	....	....	Cloudy	.030	20.939
	10 29 a.m.	14.0	758.35	Light SW ..	Cloudy, unsettled ..	.029	20.940
Dec. 14	12 01 a.m.	....	....	....	Fair	.029	20.937
	3 00 a.m.	....	....	....	Fair	.030	20.940
	9 13 a.m.	6.0	771.70	Light W ...	Cloudy, unsettled ..	.028	20.930
	9 48 a.m.	....	....	....	....	.030	20.937
Dec. 15	9 04 a.m.	3.8	767.25	Light SE...	Light snowfall in night; rains now.	.027	20.938
1912							
Jan. 2	3 59 p.m.	....	....	....	....	.032	20.905
	....	....	....	....	....	.038	20.932
Jan. 3	2 45 p.m.	3.0	763.50	Light N ...	Pleasant	.031	20.919
	....	....	....	....	....	.031	20.930
	....	....	....	....	....	.029	20.938
	4 40 p.m.	....	....	....	....	.031	20.938
Jan. 4	10 15 a.m.	—3.0	758.75	Light NE ..	Unsettled; light snow flurries.	.031	20.931
						.029	20.930
	2 00 p.m.	....	....	....		.031	20.931
	3 25 p.m.	....	....	....	....	.029	20.938
	4 00 p.m.	....	....	....	....	.032	20.933
Jan. 6	8 30 a.m.	—9.0	764.00	Brisk NW..	Sunny; clear, cold..	.029	20.933
	9 30 a.m.	....	....	....	....	.028	20.939
	10 10 a.m.	....	....	....	....	.031	20.940
Jan. 9	8 45 a.m.	0.0	737.50	Brisk W ...	Rain early a.m. ...	.029	20.940
	9 20 a.m.	....	....	....	Now colder, clearing	.029	20.941
	2 45 p.m.	—6.0	744.45	Strong W ..	Clear and cold	.028	20.933
				Average	....	.031	20.938

A result so strikingly at variance with all earlier researches must be subjected to most critical examination and control. It is possible, for example, that the apparatus was mechanically so constructed that the manometer is more readily set at zero when the mercury in the pipette *B* is at 20.94 per cent—a condition difficult to conceive, but nevertheless not absolutely impossible.

For the best proof of the accuracy and sensitiveness of the apparatus we must again turn to our analyses of cylinder air. These were made in parallel with the analyses of outdoor air and continued from April 15 to June 7, 1911. The results are given in table 62.

TABLE 62.—*Analyses made at the Nutrition Laboratory of air confined in a steel cylinder. Series 4.*

Date.	Time.	Carbon dioxide.	Oxygen.	Date.	Time.	Carbon dioxide.	Oxygen.
1911.		*p. ct.*	*p. ct.*	1911.		*p. ct.*	*p. ct.*
Apr. 15	9h06m a.m.	0.036	20.909	May 26	11h37m a.m.	0.031	20.919
	9 52 a.m.	.033	20.919		12 15 p.m.	.033	20.911
	10 24 a.m.	.033	20.911		3 27 p.m.	.035	......
	11 09 a.m.	.034	20.920		3 58 p.m.	.036	20.915
	11 46 a.m.	.033	20.912	May 27	8 28 a.m.	.035	20.899
	12 15 p.m.	.035	20.911		9 04 a.m.	.034	20.908
	2 36 p.m.	.034	20.918		9 40 a.m.	.035	20.912
	3 06 p.m.	.034	20.920		2 03 p.m.	.036	20.909
	3 51 p.m.	.034	20.919		2 42 p.m.	.034	20.911
Apr. 17	8 51 a.m.	.036	20.905		3 25 p.m.	.034	20.913
	9 31 a.m.	.034	20.921		4 07 p.m.	.033	20.910
	10 16 a.m.	.036	20.918	May 29	8 30 a.m.	.034	20.902
	10 57 a.m.	.035	20.921		10 39 a.m.	.033	20.911
Apr. 19	9 32 a.m.	.035	......		11 30 a.m.	.033	20.909
	2 27 p.m.	.036	20.918		2 02 p.m.	.032	20.908
	2 52 p.m.	.035	20.919		2 40 p.m.	.035	20.909
Apr. 22	2 00 p.m.	.030	20.905	May 31	9 21 a.m.	.048	20.903
	3 03 p.m.	.032	20.921		12 02 p.m.	.033	20.914
	3 42 p.m.	.034	20.922		2 31 p.m.	.033	20.909
Apr. 24	8 55 a.m.	.035	20.915		3 15 p.m.	.033	20.913
	9 40 a.m.	.036	20.909		4 29 p.m.	.037	20.910
	10 27 a.m.	.036	20.922	June 1	8 23 a.m.	.033	20.906
	11 04 a.m.	.036	20.919		9 18 a.m.	.034	20.907
Apr. 25	9 08 a.m.	.037	20.913		9 55 a.m.	.033	20.912
	9 50 a.m.	.036	20.920		10 39 a.m.	.035	20.907
	10 28 a.m.	.036	20.921		11 31 a.m.	.032	20.903
May 2	10 37 a.m.	.034	20.919		12 16 p.m.	.036	20.912
May 19	3 01 p.m.	.033	20.918		12 53 p.m.	.034	20.912
May 20	11 15 a.m.	.037	20.932	June 2	10 43 a.m.	.032	20.908
	2 20 p.m.	.037	20.910		11 35 a.m.	.033	20.908
	3 11 p.m.	.037	20.909		2 22 p.m.	.033	20.905
	3 52 p.m.	.038	20.913	June 3	10 23 a.m.	.035	20.910
May 22	12 37 p.m.	.037	20.910		2 28 p.m.	.031	20.912
	3 03 p.m.	.034	20.907		3 14 p.m.	.031	20.919
	3 48 p.m.	.010	20.910		3 57 p.m.	.032	20.920
May 23	10 54 a.m.	.035	20.919	June 5	8 24 a.m.	.037	20.914
	11 40 a.m.	.034	20.910		9 02 a.m.	.036	20.920
	12 20 p.m.	.033	20.919		9 43 a.m.	.034	20.911
May 24	9 22 a.m.	.034	20.909		10 30 a.m.	.034	20.918
	10 48 a.m.	.033	20.910		11 10 a.m.	.033	20.917
	11 35 a.m.	.035	20.910		4 18 p.m.	.033	20.914
	12 11 p.m.	.033	20.907	June 6	8 30 a.m.	.032	20.912
	2 48 p.m.	.032	20.909		9 10 a.m.	.033	20.912
May 25	8 41 a.m.	.032	20.909		9 54 a.m.	.031	20.913
	9 19 a.m.	.033	20.908	June 6	2 29 p.m.	.033	20.913
	11 29 a.m.	.033	20.918	June 7	8 46 a.m.	.031	20.910
	12 13 p.m.	036	20.910		9 47 a.m.	.032	20.909
	3 00 p.m.	.036	20.913		10 33 a.m.	.034	20.919
	3 46 p.m.	.035	20.910		11 13 a.m.	.034	20.918
	4 20 p.m.	.035	20.912		11 53 a.m.	.033	20.920
May 26	8 14 a.m.	.033	20.910		3 56 p.m.	.034	20.914
	9 36 a.m.	.036	20.912				

Inasmuch as the analyses indicated that the air had remained approximately constant throughout several months, it was believed that the conditions inside the cylinder were not such as to cause any material oxidation. When the air-analyses were resumed in the fall, after a summer of unprecedented heat in Boston, the oxygen percentage was found to have materially decreased. Excluding a few analyses made between September 15 and September 25, we have the results given in table 63.

TABLE 63.—*Analyses made at the Nutrition Laboratory of air confined in a steel cylinder. Series 5.*

Date.	Time.	Carbon dioxide.	Oxygen.	Date.	Time.	Carbon dioxide.	Oxygen.
1911.		*p. ct.*	*p. ct.*	1911.		*p. ct.*	*p. ct.*
Sept. 25	3^h16^mp.m.	0.032	20.872	Nov. 15	11^h26^ma.m.	0.031	20.870
	3 58 p.m.	.034	20.879		11 59 a.m.	.031	20.871
	4 39 p.m.	.034	20.892		12 34 p.m.	.032	20.871
Sept. 26	11 02 a.m.	.036	20.889	Dec. 2	9 27 a.m.	.032	20.859
	11 44 a.m.	.035	20.891		10 07 a.m.	.030	20.863
Sept. 27	9 29 a.m.	.036	20.881		10 50 a.m.	.031	20.878
Sept. 28	11 00 a.m.	.035	20.885		11 27 a.m.	.032	20.878
Sept. 29	11 15 a.m.	.034	20.882		12 03 p.m.	.032	20.876
Sept. 30	10 19 a.m.	.033	20.883		2 35 p.m.	.026	20.875
Oct. 2	10 41 a.m.	.033	20.883		3 15 p.m.	.030	20.872
Oct. 3	10 10 a.m.	.038	20.888		3 57 p.m.	.033	20.873
	10 52 a.m.	.039	20.880		4 53 p.m.	.031	20.873
	2 25 p.m.	.038	20.870	Dec. 4	9 10 a.m.	.032	20.880
	3 03 p.m.	.040	20.873		3 41 p.m.	.032	20.878
Oct. 4	2 42 p.m.	.032	20.881		4 19 p.m.	.032	20.875
Oct. 5	2 22 p.m.	.034	20.887	1912			
Oct. 6	2 34 p.m.	.032	20.881	Jan. 6	....	.032	20.860
	4 03 p.m.	.032	20.880		12 10 p.m.	.032	20.860
Oct. 25	8 54 a.m.	.021	20.873	Jan. 9	10 00 a.m.	.033	20.872
	10 10 a.m.	.034	20.873		10 40 a.m.	.033	20.862
Oct. 26	8 44 a.m.	.031	20.858		11 15 a.m.	.030	20.863
	9 21 a.m.	.035	20.861				

Of especial importance are the percentages for December 2 and 4, 1911, as they establish the absence of any effect upon the determination of carbon dioxide and oxygen resulting from the temperature of the reagents. The percentages found were constant, independent of an alteration of over 10° C. in the temperature of the water-bath, which ranged during these analyses between 20.4° C. and 32.5° C. These experiments with improved technique substantiate fully the observations on p. 97.

CONCLUSIONS FROM RESULTS WITH FIFTH ROUTINE.

From the results of analyses given in tables 61 and 62, it will be seen that the apparatus gives constant oxygen percentages for outdoor air; for any particular day or for a period of 3 or 4 days, the apparatus also gives constant results for the oxygen content of the cylinder air, although these are measurably lower than those for outdoor air. These facts demonstrate that the constant readings are not due to any peculiarity in the construction of the apparatus. Furthermore, since it is obvious from an examination of the results that there is a steady, though slight, decrease in the oxygen content of the cylinder air, the evidence in favor of both the accuracy and the sensitiveness of this apparatus becomes conclusive.

On the basis of this series of observations, then, we may state that the uncontaminated air of Boston is of constant oxygen content irrespective of conditions of weather, humidity, temperature, barometer, wind direction, and season.

It may further be stated that the percentage of carbon dioxide does not undergo any material alteration under these conditions.

And, finally, from the evidence thus secured, we may assert that in uncontaminated outdoor air the approximate percentage of carbon dioxide is 0.031 and oxygen 20.938.

ANALYSES OF AIR COLLECTED ON THE ATLANTIC OCEAN.

Since numerous writers have found noticeable differences in air collected over the sea as compared with that collected on the land, a number of samples for analysis were secured of air taken over the Atlantic Ocean. I am indebted for these samples to Mr. Harold L. Higgins, of the Nutrition Laboratory, who most carefully collected them, together with supplementary climatic data, on a sea trip between Montreal and Liverpool in November 1910. The glass sampler used was similar in form to that described by Regnault,[1] and consisted of a cylindrical tube 40 mm. in diameter and 245 mm. long, with a capacity of approximately 200 c. c. To each end of the tube was attached a short piece of glass tubing, which was drawn out in a capillary, so that when the sampler had been filled it could be sealed in the flame of a candle or an alcohol lamp. The samples were always taken on the windward side of the vessel, the sampling tubes being filled by aspiration with the mouth for a few minutes. A water-seal was provided by drawing the air first through the sampler, then through a gas-washing bottle containing water and attached by a short piece of rubber tubing, thus preventing all contamination by expired air. After sufficient aspiration the tubes were quickly taken to the stateroom and sealed, labeled, and packed in a specially constructed carrying case. No precautions were taken to dry the air before it entered the sampling tubes. Though the samples were taken in November 1910, the analyses were not made until a year later, *i.e.*, October 6 and 7, 1911. The results are presented in table 64. Aside from the constancy in the oxygen percentages, the most striking feature of the results in this table is the extraordinarily low percentage of carbon dioxide in the samples collected on November 7 and 10. In fact, all of the carbon-dioxide values are lower than normal.[2]

TABLE 64.—*Analyses of ocean air collected between Montreal and Liverpool.*

Date of collection.	Time.	Lat. N.	Long. W.	Temp. of sea-water.	Wind.	Weather.	Carbon dioxide.	Oxygen.
1910.	*p. m.*	° ′	° ′	°*F.*			*p. ct.*	*p. ct.*
Nov. 7	12h 30m	47 23	59 4	44	SE.; mod. to fresh.	Misty to foggy; overcast.	0.003	20.940
Nov. 8	12 15	45 56	51 15	48	NW.; mod..	Overcast; sea almost calm.	{ .021 { .023	20.930 20.932
Nov. 9	12 10	47 22	42 58	48	NW.; mod..	Clear, sunny; moderate sea.	.027	20.939
Nov. 10	12 15	49 21	34 39	57	S. to SW. mod.	Overcast, misty	.006	20.940
Nov. 11	12 35	50 42	25 33	55	S. to SW.; mod. only.	....Do.	.021	20.933
Nov. 12	12 25	51 10	15 56	55	SW.; mod. to fresh only.	....Do.	.024	20.940
					Average	....	....	20.936

[1] Regnault, Annales de Chimie et de Physique, 1852, ser. 3, **36**, p. 385.

[2] The injunction of Regnault (Annales de Chimie et de Physique, 1852, ser. 3, **36**, p. 392) to collect samples of dry air was unfortunately not followed. As the determination of oxygen percentages was the first consideration in this study, no especial thought was given in taking the samples to the determinations of the carbon dioxide.

A second study of ocean air was made possible through the kindness of Mr. Thorne M. Carpenter, of the Nutrition Laboratory, who carefully collected a large number of samples on a return voyage from Genoa to Boston in June 1911. Profiting by a discussion of the problem with Dr. Krogh in Copenhagen, Mr. Carpenter took special precautions to collect several samples of air dried over phosphorus pentoxide. Usually the samples were taken by aspiration with the mouth, but in collecting the dry samples it was found that the phosphorus pentoxide powder was mechanically carried to the mouth, with consequent discomfort; a rubber bulb was accordingly used. The samples were collected between June 10 and 25, 1911, but it was inexpedient to analyze them before October 14 to 26, 1911. The results of these analyses are given in table 65.

TABLE 65.—*Analyses of ocean air collected between Genoa and Boston.*

Date of collection.	Time.	Lat. N.	Long.	Barometer.	Wind.	General conditions.	Condition of sample.	Carbon dioxide.	Oxygen.
1911.		° ′	° ′	*mm.*				*p. ct.*	*p. ct.*
June 10	11h00m a.m.	.. ..	.. ..	746.0	....	Bay of Genoa	Moist ..	0.034	20.938
June 12	5 15 p.m.	.. ..	.. ..	754.1	Almost head wind; strong.	Naples; cloudless sky; temp. on deck 20–21° C.	Moist ..	.011	20.931
							Moist ..	.016	20.933
June 15	11 45 a.m.	38 47	9 04E	....	....	1st day out from Naples; moderate head sea.	Moist ..	.022	20.933
	12 00 noon	.. ..	.. ..	....	....		Moist ..	.019	20.925
								.019	20.931
June 16	11 40 a.m.	37 17	1 27E	753.8	Fair	Temp. on deck 21.5° C.; steamer going with wind; calm sea.	Moist ..	.010	20.930
	12 10 p.m.	.. ..	.. ..	....	....		Moist ..	.018	20.935
	11 50 a.m.	.. ..	.. ..	....	....		Moist ..	.012	20.932
								.017	20.938
June 17	11 40 a.m.	35 58	5 50W	752.0	Very little, if any; fresh breeze previous evening.	Clear early morning; clouded over at noon; very calm sea; temp. on deck, 20.7° C.	Moist ..	.018	20.929
June 18	....	36 40	13 11W	754.0	....	Temp. on deck in sun, 20.7° C.	Moist ..	.022	20.929
								.017	20.931
June 19	....	37 25	20 43W	....	....	....	Moist ..	.018	20.936
								.016	20.928
								.012	20.932
June 20	10 00 a.m.	.. ..	.. ..	761.0	Blowing from sea toward the shore across ship	Both samples taken at Ponte Delgada, Azores, on steamer, anchored about one-half mile from shore; temp. on deck, 20.5° C.	Moist ..	.019	20.931
								.013	20.929
June 21	12 15 p.m.	40 04	32 05W	756.5	Considerable SW. wind during night before.	Night before clear; during night, sea became rough; 6 a.m., clouded over; 7 a.m., fog; 11 a.m., quite clear.	Dry....	.031	20.930
							Dry....	.032	....
							Dry....	.031	20.931
							Moist ..	.011	20.929
							Moist ..	.018	20.938
June 22	....	41 07	40 11W	....	Changed from W. to SW.; high breeze.	Clear afternoon before; windy; moist in morning.	Dry....	.030	20.932
							Moist ..	.013	20.932
							Moist ..	.018	20.927
							Moist ..	.019	20.932
June 23	11 40 a.m.	42 18	47 42W	753.0	High SW. evening before; continued wind in morning.	Very rough sea evening before and during night; early morning, heavy rain (hail); clear about 7 to 8.	Moist ..	.018	20.929
	11 45 a.m.	.. ..	.. ..	....			Moist ..	.017	20.930
	12 30 p.m.	.. ..	.. ..	....			Dry....	.031	20.937
June 24	....	42 49	55 19W	751.0	....	....	Moist ..	.027	20.931
								.028	20.931
							Moist ..	.022	20.932
							....	.023	20.936
							Dry....	.032	20.934
June 25	....	42 42	63 33W	759.0	....	....	Moist ..	.014	20.936
							Dry....	.033	20.929
					Average	....	....	....	20.932

The wisdom of taking samples dry is seen from these results, since in all dry samples the percentage of carbon dioxide was found to be always normal. The oxygen percentages again show a striking uniformity and constancy, irrespective of geographical location, weather conditions, etc.

ANALYSES OF AIR FROM PIKE'S PEAK.

The interesting expedition to the top of Pike's Peak made by Haldane, Yandell Henderson, Douglas, and Schneider, in the summer of 1911, was utilized in that these gentlemen kindly consented to collect samples of air for this research. The apparent constancy in composition of the cylinder air during the early half of 1911 led to the belief that air samples stored in steel cylinders would not undergo a material loss of oxygen; and obviously samples collected in this way would give opportunity for innumerable analyses. Consequently three small steel cylinders, fitted with proper valves, and a strong bicycle pump were sent to Professors Haldane and Henderson. Both these gentlemen questioned seriously the advisability of using this method of sampling, and fortunately insisted upon having the usual glass samplers sent to them, in which they collected additional samples. The analysis of the air from Pike's Peak was not taken up until the fall of 1911. At this time it was found that during the summer the oxygen percentage of the air in the control cylinder had changed from 20.918 to 20.880, this not inconsiderable change possibly resulting from the extreme heat of the summer, which had been abnormal for this section. Since there had been a change in the oxygen content of this air, it was seen that no reliance could be placed upon the constancy in composition of air stored in steel cylinders, so that any results which might be obtained with air collected in this way on Pike's Peak would be vitiated. Furthermore, it could not even be assumed that cylinders filled on the same day and under the same conditions would be equal in oxidation; hence any variations from the normal oxygen content found at sea-level could not reasonably be ascribed to a persistent regular oxidation in the cylinders.

TABLE 66.—*Analyses at Nutrition Laboratory of air from summit of Pike's Peak.*

[Air collected and stored in steel cylinders.]

Data.	Carbon dioxide.	Oxygen.	Data.	Carbon dioxide.	Oxygen.
	p. ct.	*p. ct.*		*p. ct.*	*p. ct.*
Collected Aug. 6, 1911, 5 p.m. Wind, moderate N.W. Weather clear.	0.034	20.915	Collected Aug. 8, 1911, 5 p.m. Wind, moderate N.W. Weather clear.	0.031	20.881
	.032	20.918		.032	20.883
	.031	20.914		.032	20.880
	.036	20.923		.035	20.886
	.034	20.922		.033	20.887
	.036	20.928		.032	20.889
	.038	20.929			

The samples of air collected in the steel cylinders were analyzed between September 20 and October 5. While the results have but little value, they are given in table 66 as a further demonstration of the inadequacy of this method of preserving air samples. The very large differences in the oxygen content of the two cylinders bears out the belief that the

oxidation may be very irregular. The percentage of carbon dioxide is slightly higher than normal, but whether this is due to oxidative processes in the cylinder, to organic matter from the lubrication and rubber hose of the bicycle pump, or to an actual condition of the air, the results do not show.

The samples collected in glass tubes were analyzed October 9 and 10, 1911, the results in table 67 being obtained. Although some samples stored in glass have a strong tendency to decrease in the percentage of carbon dioxide, these analyses show a percentage which is approximately normal. With the exception of the results obtained for August 14, the oxygen percentages are also normal. While apparently there is a slight diminution in the percentage of oxygen, the average, 20.927 per cent, is obviously affected by the results for August 14, and since at least one analysis on each of the three days showed a percentage of 20.930 or over, it seems hardly probable that this apparent slight decrease is significant.

TABLE 67.—*Analyses made at the Nutrition Laboratory of air collected on summit of Pike's Peak—4312 meters.*

[Air collected and stored in glass samplers.]

Date of collection.	Time.	Barometer.	Wind.	Weather.	Carbon dioxide.	Oxygen.
1911.		*mm.*			*p. ct.*	*p. ct.*
Aug. 11	$6^{h}00^{m}$p.m.	459	Strong W...	1 hr. after snowstorm with much lightning.	0.027	20.928
	6 00 p.m.	459	....Do....		.032	20.936
Aug. 11	9 00 p.m.	459	....Do....	Somewhat clearer; 32° F.....	.030	20.932
	9 00 p.m.	459	....Do....		.028	20.930
Aug. 12	10 00 a.m.	458	....Do....	Partly sunshine, partly driving clouds; beginning to clear and wind falling.	.029	20.930
Aug. 14	8 30 a.m.	462	Gentle N...	Beautiful clear day; day and night before clear and warm.	.031	20.911
	8 30 a.m.	462	....Do....		.029	20.923
Aug. 14	5 30 p.m.	462	Very light NE.	....	.031	20.932
	5 30 p.m.	462	....	....	.029	20.921
			Average	....	....	20.927

ANALYSES OF STREET AIR.

While the air in the vicinity of the laboratory would be expected to be somewhat contaminated with carbon dioxide and consequently deficient in oxygen, it is obvious that the contaminating factors are not of sufficient magnitude to affect perceptibly the analytical results. It became a question of interest, however, as to how far one must go into the heart of the city to secure air of less than normal oxygen content. Two samples were therefore collected, in containers fitted with excellent glass stop-cocks, from a crowded business street. The results of the analyses are given in table 68.

The percentage of oxygen was slightly, though almost imperceptibly, less than that in normal air, while the carbon dioxide was slightly higher than the average normal. Since by reference to table 61 it can be seen that the samples analyzed at the laboratory on the same date showed 20.939 per cent of oxygen and 0.029 per cent of carbon dioxide, it can be

safely asserted that this apparatus was sufficiently sensitive to show even the slight contamination produced by the congestion of population in a narrow city street. It is also remarkable that under these conditions the carbon-dioxide increment and oxygen deficiency were not very much greater. Observations such as these tend to demonstrate the extent of the diffusion of gases and the establishment of equilibrium by air-currents.

TABLE 68.—*Analyses made at the Nutrition Laboratory of air collected on a crowded business street in Boston.*

Date.	Time.	Barometer.	Temperature.	Place.	Carbon dioxide.	Oxygen.
1911.	*p. m.*	*mm.*	°C.		*p. ct.*	*p. ct.*
Nov. 14	1h30m	769.55	2.7	In Washington st. between	0.031	20.930
				Summer and Avon sts....	.032	20.929
Nov. 14	1 40	769.55	2.7	In Washington st. between	.032	20.929
				Summer and Franklin sts.	.034	20.929

ANALYSES OF SUBWAY AIR.

Although foreign to the major question here studied, namely, the composition of uncontaminated air, it was also of interest to find out to what extent the air was vitiated in the modern "tube" or "subway" so extensively used for suburban passenger traffic. Two samples taken simultaneously at the Park Street station in the Boston subway gave the results presented in table 69.

TABLE 69.—*Analyses made at the Nutrition Laboratory of air collected at the Park Street station of the Boston subway.*

Date.	Sample.	Time.	Carbon dioxide.	Oxygen.
1911.			*p. ct.*	*p. ct.*
Oct. 25	I	9h30ma.m.	0.064	20.903
			.062	20.898
Oct. 25	II	9 30 a.m.	.065	20.897

The samples were taken immediatedly after the "rush hours" were ended and when the oxygen content of the air in the subway might be expected to be at a minimum. The fall of approximately 0.03 per cent in oxygen is accompanied by a rise of 0.032 per cent in the carbon dioxide. Here again one is divided between appreciation of the extraordinary sensitiveness of the Sondén apparatus and surprise that the circulation of air in the subways can be so good and the diffusive power of air so extended that the increases in carbon dioxide and decreases in oxygen are of such slight amount.

Thanks to the kindness of Dr. E. F. DuBois and Dr. Warren T. Coleman, two specimens of air were collected from the subway in New York City. The results, which are given in table 70, differ in no wise from those found in the Boston subway and show an increase in carbon dioxide and decrease in oxygen infinitely less than one would normally have expected.

TABLE 70.—*Analyses made at the Nutrition Laboratory of air collected in the subway, in New York City.*

Date.	Time.	Place.	Carbon dioxide.	Oxygen.
1911.			*p. ct.*	*p. ct.*
Nov. 21	6^h03^mp.m. (rush hour)	Grand Central subway station	0.061	20.900
Nov. 21	5 52 p.m.	Between 110th and 96th sts.......	.071	20.897

The results of this series of experiments have a particular value, inasmuch as they show clearly that a decrease in oxygen is accompanied by an approximate increase in carbon dioxide. While the measurement of carbon dioxide has been taken as an index of good or bad ventilation, the fact that the proportion of oxygen is actually lowered by an increase in the carbon dioxide has never before been clearly demonstrated. As a result of this study, however, knowing both the constancy of oxygen in outdoor air and the sources of carbon-dioxide production, and knowing also that with the carbon-dioxide production there must likewise be an oxygen consumption, we can safely state that for every one-hundredth per cent of increase in carbon dioxide there will be approximately one-hundredth per cent decrease in oxygen.[1] It will be seen, therefore, that since there are a number of simple and accurate methods for determining carbon dioxide, the time-consuming and complicated determinations of oxygen are entirely unnecessary, as the determination of the percentage of carbon dioxide in the air establishes the approximate percentage of oxygen.

ABSORPTION OF OXYGEN BY POTASSIUM PYROGALLATE.

Since the constancy of the oxygen content of the air has been demonstrated in this research, it has been possible to make a more accurate study than heretofore of the conditions affecting the absorption of oxygen by potassium pyrogallate. Many investigators have experimented with potassium pyrogallate as an absorbing agent for oxygen; but inasmuch as there appeared to be fluctuations in the oxygen content of the air, they have sought for the maximum absorption capacity and minimum production of carbon monoxide without attempting to control the absorption of oxygen. Particularly confusing has been the fact that the potassium hydroxide as found on the market varies greatly in its water content, the amount ranging from 5 to 25 per cent.

To investigators on this subject, the experience of Haldane and Hempel has been of the most interest. As already stated, the use in this research of Haldane's saturated solution of potassium hydroxide for dissolving the pyrogallol did not seem wise with so delicate an apparatus as ours. Should there be a complete solidification of the reagent in chamber *D*, considerable time would be required to get the solution again in con-

[1] The one inexplicable phenomenon is the abnormally high percentage of carbon dioxide found in the air of Greenland by Krogh.

dition for use; this would result in delay, with always a possibility that the expansion might fracture the glass vessel. Furthermore, as the slightly more dilute solution ultimately used for the routine analyses was so much stronger than the solution recommended by Hempel, it was thought that the coefficient of absorption rather than the completeness of absorption would be sacrificed by employing a less concentrated solution.[1] In the supplementary study made of the comparative value of the various potassium pyrogallate solutions, the formulas recommended by both Haldane and Hempel were tested as to their absorptive powers. In all, four different solutions were used:

(1) Hempel's solution, prepared according to his formula. Five grams of pyrogallol were dissolved in 15 c. c. of water and mixed with 120 grams of potassium hydroxide dissolved in 80 c. c. of water. Stick potassium hydroxide not purified by alcohol was used in all the solutions.

(2) Hempel's solution, prepared by a modified formula. Inasmuch as stick potassium hydroxide contains from 5 to 25 per cent of water, instead of using 120 grams of stick potassium hydroxide as in the first solution, only sufficient was used to be equivalent to 120 grams of anhydrous potassium hydroxide. To maintain the proper proportion of water, the amount in the stick caustic potash was included in the 80 grams required by Hempel's formula. As the particular lot of stick caustic potash in use at that time was found by alkalimetry to contain 92 per cent of potassium hydroxide, 130 grams of this chemical was mixed with 70 c. c. of water and subsequently the 5 grams of pyrogallic acid added.

(3) The potassium pyrogallate solution used throughout this research. This is described on p. 80.

(4) Haldane's formula, requiring a saturated solution of potassium hydroxide in water, with a specific gravity of 1.55. The solution is made in the proportion of 1 gram of pyrogallic acid to 10 c. c. of the potassium-hydroxide solution and hence has the greatest density of all the solutions.

For purposes of comparison, both outdoor air and cylinder air were analyzed in this study, exactly the same routine being followed in all analyses, and with all four solutions. (See p. 100.) The results are incorporated in table 71.

The results of these two series of analyses point conclusively to marked differences in the results obtained with solutions of varying strength. These differences may be attributed either to an incompleteness of absorption or to the formation of carbon monoxide. That incompleteness of absorption by the weaker solutions can account in any measure for the differences here observed seems hardly probable when the analyses for January 26, 1912, are considered. The results obtained on that date show that extending the time during which the air was in contact with the reagent for an additional 12 minutes made barely an

[1] For a criticism of the use of potassium pyrogallate as an absorbent of oxygen, see B. Tacke, Archiv für die gesammte Physiologie, 1886, 38, p. 401.

appreciable increase in the percentage of oxygen. Furthermore, for fear that simple contact might be inefficient, as a further precaution, in certain analyses on January 31 and February 1, the gas was passed into the potassium pyrogallate 10 times at the end of the regular routine, but with no appreciable increase in oxygen percentage.

TABLE 71.—*Results of comparative study of oxygen absorption by potassium pyrogallate solutions of varying concentration.*

Date.	Outdoor air.				Cylinder air.			
	Hempel solution. I.	Hempel solution. II.	Regular solution.	Haldane solution.	Hempel solution. I.	Hempel solution. II.	Regular solution.	Haldane solution.
1912.	*p. ct.*	*p. ct.*	*p. ct.*	*p. ct.*	*p. ct.*	*p. ct.*	*p. ct.*	*p. ct.*
Jan. 6	....	....	20.933 20.939 20.940	....	....	.....	20.860 20.860	....
Jan. 9	....	....	20.940 20.941 20.933	....	....	....	20.872 20.862 20.863	....
Jan. 26	20.848 20.849 20.843 [1]20.857 [1]20.852 [1]20.854 [1]20.852	....	....	....	20.759 [1]20.773	....	....	....
Jan. 27	....	....	....	20.952 20.958 20.950 20.950 20.952	....	....	....	20.879 20.878 20.875
Jan. 30	....	20.910 20.917 20.918 20.910 20.911	....	....	....	20.828 20.830 20.832	....	....
Jan. 31	....	....	....	20.949 20.958 [2]20.953 [2]20.960 [2]20.975	....	....	....	....
Feb. 1	....	....	....	20.958 [2]20.961 [2]20.954 [2]20.954	....	....	....	....
Average	20.851	20.913	20.938	20.956	20.766	20.830	20.863	20.877

[1] These were given an additional 12 minutes in the potassium-pyrogallate solution.

[2] After absorbing the oxygen in the regular way, the air was sent back and forth into the potassium-pyrogallate solution 10 times before the reading was taken.

Since the obvious inference is that there must have been a slight formation of carbon monoxide with the weaker solutions, one questions immediately if it is certain that even with the strong Haldane solution there may not be traces of carbon monoxide. Haldane's experience in detecting minute amounts of carbon monoxide goes a long way, however, in establishing faith in his assertion that not the slightest trace is found with the use of his concentrated solution.

CONCLUSIONS.

(1) *Apparatus for gas-analysis.*—The Sondén apparatus here described fulfills all conditions essential to exact gas-analysis, save that the gas is not measured dry in a dry pipette over mercury. In spite of this one drawback, the technique has been developed so as to insure a constancy and sensitiveness found as yet in no other form of gas-analysis apparatus.

(2) *Reagent for the absorption of oxygen.*—Experimentation with all forms of absorbents for oxygen, including several strengths of potassium pyrogallate solution, leads inevitably to the conclusion that the Haldane potassium-pyrogallate solution is the most efficient agent thus far recommended. The analyses of those investigators employing phosphorus or sodium hydrosulphite do not lead one to believe that for efficiency they can supersede the Haldane solution.

(3) *The constancy of the oxygen percentage in outdoor air.*—The results of analyses of air taken near the laboratory showed no material fluctuation in oxygen percentage during a period extending from April 15, 1911, to January 30, 1912. This constancy was maintained in spite of all possible alteration in weather conditions, changes in barometer, thermometer, humidity, and wind direction and strength; furthermore, the experiments were made before, during, and after the vegetative season. The average result of 212 analyses showed 0.031 per cent of carbon dioxide and 20.938 per cent of oxygen. The analyses of air collected over the ocean, at two different times of the year, and on the top of Pike's Peak, gave essentially similar results. The average results of all the analyses made in this research of outdoor air are summarized in table 72.

TABLE 72.—*Summary of analyses made at the Nutrition Laboratory of outdoor air.*

	Number of analyses.	Carbon dioxide.	Oxygen.	Oxygen[1] (corrected).
		p. ct.	*p. ct.*	*p. ct.*
Air near laboratory	212	0.031	20.938	20.952
Ocean air (Montreal-Liverpool)	7	....	20.936	20.950
Ocean air (Genoa-Boston)	36	....	20.932	20.946
Pike's Peak	9	....	20.927	20.941

[1] A correction of 0.014 has been added to the average results obtained in this research to make them comparable with results secured with the Haldane solution. (See p. 113.)

(4) *The absolute oxygen content of outdoor air.*—While this research has dealt mainly with comparative values, certain fundamental difficulties in method and technique prevent deductions with regard to the absolute oxygen content of outdoor air. The use of the Haldane concentrated potassium-pyrogallate solution would seem to preclude the possibility of the formation of measurable amounts of carbon monoxide, but we always have to deal with the possible error in the water adhering to the pipette when the change in level of the mercury is made. Since the contraction in volume is assumed to be only that due to absorbed oxygen, and since unquestionably some water is confined between the

glass and the mercury, the contraction as measured is invariably too large by the volume of the water so held. Unfortunately no quantitative measurements of this water are possible with the Sondén apparatus. In this study, however, we have aimed to secure constancy in the amount of water thus trapped, knowing that the absolute amount could not be measured. The analyses of both outdoor and cylinder air with the potassium pyrogallate employed in this research, as well as the analyses made with Haldane's strong solution, showed invariably that the correction of +0.014 should be added to the results given to make them comparable with analyses made with the Haldane solution.

The atomic weights of but few of the chemical elements are known to 1 part in 2000, and hence it may now rightly be said that air is a physical mixture with the definiteness of composition of a chemical compound.

(5) While the combustion of fuel and the vital processes of men and animals result in a local increase in carbon dioxide and decrease in oxygen on the one hand, and vegetable growth results in a decrease in carbon dioxide and increase in oxygen on the other, the extraordinary rapidity with which the local variations in the composition of the air are equalized is accentuated by the observations on street air, which show but the slightest trace of an oxygen deficit.

The ratio between the increment in carbon dioxide and the decrease in oxygen leads naturally to the conclusion that carbon-dioxide determinations may be taken as excellent indications of the oxygen content and thus the necessity for elaborate and time-consuming oxygen determinations disappears. For every 0.01 per cent increase in the atmospheric carbon dioxide, one may safely assume a corresponding decrease in the percentage of oxygen.

NUTRITION LABORATORY OF THE CARNEGIE INSTITUTION OF WASHINGTON,
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